Investigation of Effective Odor Control Strategies
Final Report

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Report # (leave blank)

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FINAL (ANNUAL) REPORT

12/01/2015 – 02/28/2018

PROJECT TITLE: Investigation of Effective Odor Control Strategies

PRINCIPAL INVESTIGATOR(S): Daniel E. Meeroff, Ph.D.

AFFILIATION: Florida Atlantic University

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PROJECT WEBSITE: http://labees.civil.fau.edu/leahcate.html

COMPLETION DATE: 01/31/2018

TAG MEMBERS: Mark Eyeington, Mark Maclean, Mark Bruner, Owrang Kashef, D.V. Reddy, Craig Ash, Ravi Kadambala, Ron Schultz, Jeff Roccapriore, André McBarnette, Dan Schauer, Damaris Lugo, Amanda Krupa, Richard Meyers, Amede Dimonnay, Art Torvela, Ted Batkin, Roshan Jachuk, Fred Bloetscher, Patrick Carol, Joseph Lakner, Kevin Leo, Hala Sfeir, Rebecca Rodriguez, Myles Clewner

KEY WORDS: Odor, meteorological conditions, landfills, biosensor, odor binding protein

ABSTRACT: Nuisance odor levels produced by solid waste management operations such as landfill facilities, wastewater treatment plants and confined animal feeding operations are subject to regulatory standards because of their impacts on the quality of life of the public living within range. Failure to meet such standards may result in costly fines, litigation, inability to acquire permits, mitigation, and re-siting operations. Since measurement of environmental nuisance odors is currently limited to subjective techniques, monitoring odor levels to meet such standards is often problematic. The objective of the proposed research is to investigate the conditions that impact odor complaints and to develop a standardized, non-subjective measurement of nuisance odors using human odorant binding protein 2a (OBP2A) or similar analog. Since OBP2A binds a wide range of odorants, it may be used singularly as an odorant detection method for municipal solid waste facilities whose odors are caused by a vast array of chemicals in varying proportions.

METRICS:

1. List graduate or postdoctoral researchers **funded** by **THIS** Hinkley Center project.

Last name, first name	**Rank**	**Department**	**Professor**	**Institution**
Roblyer, Julia	MSCE Candidate	CEGE	Meeroff	FAU
Vidovic, Mateja	MSCE Candidate	CEGE	Meeroff	FAU

2. List undergraduate researchers working on **THIS** Hinkley Center project.

Last name, first name	**Department**	**Professor**	**Institution**
Martinez, Angel	CEGE	Meeroff	FAU

3. List research publications resulting from **THIS** Hinkley Center project.

None yet

4. List research presentations resulting from **THIS** Hinkley Center project

3 TAG meetings

Roblyer, J. and Meeroff, D.E. (2017). Biosensor development for odor measurement. Florida Southeast Chapter of Air and Waste Management Association. January 17, 2017.

5. How have the research results from **THIS** Hinkley Center project been leveraged to secure additional research funding?

A proposal was submitted to EREF in August 2016: "Detection of nuisance odors using fluorescently labeled odor binding proteins," EREF, $175,000, August 2016. Result: Selected for final group but not funded.

A proposal was also submitted to EREF in December 2016: "Detection of nuisance odors using odor binding protein biosensor," EREF, $169,569, December 2016. Result: Funded at $150,000.

A proposal was also submitted to the Hinkley Center in December 2016: "Year 2: Investigation of Effective Odor Control Strategies," Hinkley Center, $56,097, April 2017. Result: Funded at $50,487 with stipulation to change the title to: "Development of an analytical biosensor for measuring odorants in the ambient air near solid waste management facilities."

6. What new collaborations were initiated based on **THIS** Hinkley Center project?

Dr. Jason Hallstrom (FAU I-SENSE Center), Dr. Binninger (FAU College of Science), Craig Ash and Jim Christiansen (Waste Management), Dick Pope (Hazen and Sawyer), Robert Bowker (Bowker and Asoociates), Philip Wolstenholme (Brown and Caldwell), Chris Hunniford (V&A Consulting Engineers), and Bruce Singleton (CDM Smith), Dr. Loic Briand, Research Director of the Center for Taste and Feeding Behaviour in Dijon, France, Artur Ribeiro, Professor of Biological Engineering at the University of Minho in Braga, Portugal, and Dr. Chelsea Smartt, Associate Professor of UF's Florida Medical Entomology Laboratory.

7. How have the results from **THIS** Hinkley Center funded project been used (not will be used) by FDEP or other stakeholders? (1 paragraph maximum).

To date, the results have not been used by stakeholders; however, a progress report presentation was made to Waste Management personnel to show the results of preliminary analysis of odor complaints relationship with meteorological data. We plan to continue to work with our partners to share our results and refine how odor complaints are dealt with by the industry.

EXECUTIVE SUMMARY

12/01/2015 – 02/28/2018

PROJECT TITLE: Investigation of Effective Odor Control Strategies

PRINCIPAL INVESTIGATOR(S): Daniel E. Meeroff, Ph.D.

AFFILIATION: Florida Atlantic University

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COMPLETION DATE: 01/31/2018

In 2015, the Bill Hinkley Center for Solid and Hazardous Waste Management funded FAU Lab.EES to find ways to improve and standardize odor identification, evaluate additional methods to establish reasonable, objective standards for odor severity, and explore other options for mitigation and detection including a novel technology that will attempt to use human odorant binding protein to quantify odors. Areas of application include policy development, land use strategic planning, odor regulation, complaint assessment, odor impact assessment, odor master planning, odor control efficiency assessment, and process design.

Nuisance odor levels produced by solid waste management operations such as landfill facilities, wastewater treatment plants and confined animal feeding operations are subject to regulatory standards because of their impacts on the quality of life of the public living within range. Failure to meet such standards may result in costly fines, litigation, inability to acquire permits, mitigation, and re-siting operations. Since measurement of environmental nuisance odors is currently limited to subjective techniques, monitoring odor levels to meet such standards is often problematic.

The objective of the proposed research is to develop a standardized, non-subjective measurement of nuisance odors using human odorant binding protein 2a (hOBPIIA) or similar analog. Since hOBPIIA binds a wide range of odorants, it may be used singularly as an odorant detection method for municipal solid waste facilities whose odors are caused by a vast array of chemicals in varying proportions.

The hOBPIIA was synthesized and isolated using standard laboratory methods. Following isolation, hOBPIIA was labeled with fluorescent markers (1-AMA) to indicate when odorant molecules were bound to the protein. After fluorescent marking, hOBPIIA was exposed to known concentrations of H_2S within a vacuum chamber. Fluorescence was measured using a fluorometer and analyzed for concentration-dependence during odorant binding. The relationship followed an inverse Beer's Law correlation, such that the concentration of hydrogen sulfide can be accurately determined using fluorometric measurements.

1. INTRODUCTION

1.1 BACKGROUND

Dealing with nuisance odor emissions is one of the critical challenges facing the solid waste management industry today. Production of malodorous compounds from landfill operations prior to processing is largely inevitable due to the nature of the waste and the anaerobic decomposition of the readily biodegradable components (Clark 2009). Ritzkowski et al. (2006) indicated that emissions of gaseous pollutants, produced in landfill sites and solid waste operations, can last up to 30-100 years after the landfill is technically closed. Odors are particularly difficult to manage due to the very low threshold concentrations of odor contributing compounds typically found in solid waste operations (Southamton 2013). The public perception is that if odors can be detected, then those odors must automatically be harmful to human health (Razato et al. 2012). Further complicating matters is the subjective nature of odor detection, which makes objective surveillance and quantification nearly impossible.

Ideally, solid waste management facilities are to be located far from further human contact, but population growth, sprawling development, and transportation optimization have led to public encroachment in areas surrounding urban solid waste facilities, with this essential infrastructure now having to operate in closer proximity to potential receptors than initially intended. This situation can lead to sharp increases in odor complaints (Schiffman et al. 2000; De Feo, De Gisi and Williams 2013). Nuisance odors may even impact the ability to meet permit obligations, potentially leading to hundreds of millions of dollars in re-siting, litigation, enforcement, and mitigation. However, odor complaints are largely based upon highly subjective information and regulatory standards that are increasingly difficult to meet, even for the most responsible facility managers. This trend will continue until a viable solution can be found.

The fugitive nature of odors makes it very difficult to intercept and manage, since transport across considerable distances can happen in a matter of minutes from the source, depending on many different environmental factors including source strength, weather patterns, wind speed and direction, and topographical features (Brozozowski 2017). Odors are greatly affected by atmospheric conditions and diluted in response to local winds. Solid waste facilities want to be a good neighbor and by identifying proper mitigation strategies, odors can be prevented, minimized and managed. Complex atmospheric conditions and local winds have the potential to affect the strength of odors perceived in the field (Zeiss et al. 1993; Sarkar et al. 2003; Larro et al. 2004; Wenjing et al. 2015). Some meteorological conditions tend to increase the strength of odors, while others facilitate odor dispersal from landfill sites (McKendry, Looney, and McKenzie 2002). With all of that being said, relatively little can be done by solid waste managers to modify the climate or microclimate.

Citizen odor complaints can seem to be an inconvenience for solid waste facilities, but actually they can be used as a tool for identifying sources of odors and improving day-to-day operations. Also, odor complaint data logs, if collected properly with relevant information on meteorological conditions, odor characteristics, and location at the time of occurrence, can help with correlating odors to key meteorological parameters to determine the conditions that influence the strength and dispersion of odors downwind to communities (McKendry et al. 2002).

Key meteorological parameters such as temperature, humidity and pressure are known to influence the emissions of odors (Che et al.2013; Capanema et al. 2014), while wind speed and wind direction are responsible for dispersion of odors downwind to residential areas (Qdais 2007; Air Quality Management District 2009; Ying et al. 2012). Clearly nuisance odor issues represent a major challenge for urban solid waste facilities; however, odor science is still not completely understood, and current odor measurement techniques are subjective or largely inaccurate. Information on how the frequency of odor complaints is related to meteorological conditions is needed to better understand how to manage and mitigate offsite odor migration. Furthermore, a revolutionary new analytical technology is also needed so that the industry can better respond to odor issues with improved certainty and regulatory clarity, saving resources and repairing confrontational relationships with community neighbors.

1.2 MAJOR ODOR SOURCES AT THE LANDFILL

In many parts of the world, landfilling has been the most common method for solid waste disposal (El-Fadel, Findikakis, & Leckie 1995; USEPA 2017; Freudenrich 2017), because it is capable of safely disposing of solid waste by preventing further human contact and preventing groundwater contamination when operated properly under ideal conditions. However, landfilling is not without its challenges. Gases are formed when buried wastes decompose (breakdown by bacteria) or volatize (change from a liquid or solid to a vapor). Although the natural processes that create these gases are unlikely to pose any serious health hazards, they may cause odors that some people find unpleasant. The main sources that generate odors at landfills are landfill gas (LFG), leachate, raw municipal solid waste (MSW), and/or biosolids at the active working face or on the tipping floor. LFG is produced due to: 1) anaerobic decomposition of waste to generate methane and smaller amounts of hydrogen sulfide and other known odorants (El-Fadel, Findikakis, & Leckie 1995), 2) volatilization of chemical constituents that occurs when wastes transform from a liquid or solid to a vapor, and 3) chemical reactions that take place when waste is mixed together in disposal operations (MassDEP 2007). If not managed properly, MSW disposed of at the active face can be responsible for the production of nuisance odors while diffusing gas emissions to the atmosphere (Chemel et al. 2012).

Some solid waste operational activities also contribute to odor impacts at landfills. Drilling in the waste mass to construct landfill gas collectors can result in fugitive emissions escaping through the borehole while open to the atmosphere (USEPA 2000). A similar scenario occurs when excavating trenches (McKendry et al. 2002), where odors also can escape the landfill body while exposed to atmosphere. Insufficient vacuum on the landfill while extracting landfill gas could also cause escape of odors. Type and thickness of cover (Anunsen 2007; Santonastaso et al. 2014) is of great importance since adequate cover (daily or intermediate) ensures that gases (and odors) do not escape. Waste receiving and processing activities are another potential source of odors, since work at the landfill active area may cause odor emissions until the waste is spread, compacted and covered (McKendry et al. 2002; Clark 2009; Personal communication with site personnel). Overly odorous loads, such as household garbage or wastewater treatment biosolids, papermill sludge, and other waste products are all potential contributors to nuisance odors (Personal communication with site personnel). Leachate seeps may also be an odor source (NSWMA 2008; Golder Associates Inc. 2010; Palmiotto et al. 2014; Personal communication with site personnel). If there is too much water in the landfill, it will clog collectors while reducing the ability to remove LFG, which results in higher odors. In general, odors produced by leachate are formed when water from precipitation flows through the MSW in a landfill cell and

transports odors from the waste itself. If the leachate collection system is not operating appropriately, odors can escape through manholes or be carried to the atmosphere by venting, and then migrate offsite (NSWMA 2008). Odors generated within the landfill itself can escape through the cover, through cracks, through LFG wells, and through lateral migration (Yazdani 2015). A summary of some of the solid waste operational activities that could contribute to odor is presented in Table 1.

Table 1. Operational activities that typically contribute to odors (personal communication with two different landfill partners participating in this study).

Operational Activities	Contribution to Odor
Drilling in the waste mass to construct landfill gas collectors	Odors escape through the borehole while open the atmosphere
Excavating trenches in waste to install horizontal gas collectors	Odors escape while trench is open to atmosphere
Insufficient vacuum on the landfill to extract gas	Odors escape as fugitive emissions
Inadequate cover (daily or intermediate), cover type and thickness	Odors escape from higher pressure inside the landfill to lower atmospheric pressure through cracks or weaknesses in the cover
Leachate seeps	Odors escape with the leaking of fluids out of the waste along the slopes
Collector clogging caused by too much water in the landfill	Odors escape with gas well condensates or build up in areas that are clogged and find a different way to the surface or release to the atmosphere
Waste receiving and processing activities	Waste has odor when delivered to the landfill active area and may cause odors until the waste is spread, compacted and covered
Overly odorous loads	Waste has odors associated with household garbage, biosolids, sludges, RSMs, etc.

Generation of LFG depends on the type of waste present in the landfill and the age of the landfill, as well as the environmental conditions such as oxygen levels, temperature, moisture content, pH, alkalinity, composition of daily cover, and the physical compression density of the waste (Yazdani 2015). Methane and carbon dioxide are two main components of landfill gas which typically account for 90% of the total gas produced (El-Fadel et al. 1997; Tchobanoglous & Kreith 2002; Dincer et al. 2006; Golder Associates Inc. 2010), and both are odorless so neither contributes to landfill odor complaints. Nitrogen and oxygen are usually present in small amounts in LFG, mainly as a result of air being trapped within the waste, and both are also odorless (El-Fadel et al. 1997). Table 2 summarizes the composition of typical LFG.

Table 2. Typical Landfill Gas Composition (El-Fadel, Findikakis, & Leckie 1995)

Component	**Concentration Range** *Percent Dry Volume Basis*
Methane	40 – 70
Carbon Dioxide	30 – 60
Nitrogen	3 – 5
Oxygen	0 – 3
Carbon Monoxide	0 – 3
Hydrogen	0 – 5
Hydrogen Sulfide	0 – 2
Trace Compounds	0 – 1

Since the four main components of LFG found in Table 2 are essentially odorless, the odor originates from the trace compounds and other minor constituents. This means that less than 2% (H_2S and trace compounds) is culpable for nuisance odors associated with landfills. Many known odorants and hydrocarbons are present in relatively trace amounts (refer to Table 3).

Table 3. Typical Trace Compounds in LFG (El-Fadel, Findikakis, & Leckie 1995)

Component	**Concentration Range** *mg/m^3*
Alcohols	2 – 2500
Organosulphur Compounds	3 – 240
Halogenated Hydrocarbons	1 – 2900
Aromatic Hydrocarbons	30 – 1900
Aldehydes	0 – 200
Ketones	0 – 50
Hydrocarbons • Alkanes • Cycloalkanes • Alkenes • Others	 • 20 – 4500 • 1 – 1000 • 6 – 1100 • 8 – 600
Esters	0 – 1300
Ethers	0 – 250

1.3 ODOR CAUSING COMPOUNDS

Nuisance odors are mostly the result of relatively low concentrations of odor causing compounds (esters, hydrogen sulfide, organosulfurs, alkylbenzenes, limonene, and other hydrocarbons) in LFG released to the ambient air (El-Fadel et al. 1997). A large variety of odor causing compounds (more than 300) have been recognized in landfill gas (McKendry et al. 2002; Anunsen 2007; Ko et al. 2015). Nuisance odors are most often related to sulfur-containing compounds, essentially mercaptans and sulfides, especially hydrogen sulfide (McKendry et al. 2002). Also, ammonia is

often identified as responsible for causing odors in landfill gas (Henry & Gehr 1980; Kim et al. 2005; Romain et al. 2005; Ko et al. 2015). Ammonia is a characteristic product of protein degradation. It is a colorless gas with a pungent odor (Romain et al. 2008; Ko et al. 2015). It does not linger in the atmosphere since it breaks down readily in water and evaporates quickly (Chen et al. 2003).

Hydrogen sulfide is generated when sulfate is biologically reduced, producing a strong, "rotten egg" smell. It is toxic and poses a threat to landfill gas-to-energy equipment because it is corrosive (Fairweather & Barlaz 1998). Hydrogen sulfide is often associated with construction and demolition debris (C&D), as well as with recovered screen material (RSM) from screening mixed C&D, since biodegradation of gypsum drywall, a primary component of C&D debris, is identified as a major cause of hydrogen sulfide production (Yang et al. 2006). A study by Cooper et al. (2011) measured concentrations of hydrogen sulfide in the ambient air at several locations around a C&D landfill located in Central Florida. Measured concentrations were used to estimate hydrogen sulfide emission rates that were used to model odor buffer distances (marked as "red", "yellow" and "green" zones). The model used in the study was the American Meteorological Society/Environmental Protection Agency Model (AERMOD). Model inputs require relevant meteorological conditions such as: wind direction, wind speed and stability class. For higher accuracy, at least one-year of hourly meteorological data and multiple in-situ H_2S emission rate measurements are necessary (Cooper et al. 2011).

Some odorants are detectable at different concentrations. The level at which odors are first detected by the human nose is called the odor detection threshold (ODT), and it varies from person to person. Odor thresholds for hydrogen sulfide and ammonia, as well as other odorants with different character categories typically observed around landfills are presented in Table 4.

Table 4. Odor Detection Threshold of Selected LFG Odor Causing Compounds (McKendry, Looney and McKenzie 2002).

Odor Compound	Reported Concentration in LFG *(mg/m^3)*	Reported OTD Range *(mg/m^3)*
Butanoic Acid	0.1 – 210	0.0000029 – 9
Butyl Mercaptan	0.01 – 16.1	0.006 – 12
Diethly Disulfide	0.1 – 1.0	0.0003 – 0.02
Dimethly Disulfide	0.02 – 40	0.00023 – 12
Dimethyl Sulfide	0.02 – 135	0.00033 – 0.6
Ethyl Mercaptan	0.1 – 120	0.00025 – 0.001
Methyl Mercaptan	0.005 – 430	0.0000003 – 0.02
Ethyl Butanoate	0.1 – 350	0.00003 – 0.28
Hydrogen Sulfide	0.0005 – 97,152	0.0001 – 2.8
Methyl Butanoate	0.2 – 125	0.0019 – 0.077
Propyl Mercaptan	0.05 – 2.1	0.0000025 – 0.00014
Xylene	0.0015 – 1100	0.0002 – 100

Hydrogen sulfide odors can be detected at relatively low levels in the air (0.5 – 1.0 ppb; 0.00075-0.0015 mg/m^3), well below the limit that would pose a threat to human health of 30 mg/m^3 by the

Occupational Safety and Health Administration (OSHA) and 15 mg/m^3 by the National Institute for Occupational Safety and Health (NIOSH) (ATSDR 2017). Common odor causing compounds in solid waste operations and their odor thresholds are presented in Table 5.

Table 5. Common Odor Causing Compounds in Landfill Gas (ATSDR 2016)

Component	Odor Description	Odor Threshold *(mg/m^3)*	Odor Threshold *(ppb)*
Hydrogen Sulfide	Strong rotten egg	0.00075 – 0.0015	0.5 – 1
Ammonia	Pungent acidic or suffocating	0.75 – 3.75	1000 – 5000
Benzene	Paint thinner-like	2.89	840
Dicholoethylene	Sweet, ether-like, slightly acrid	0.363	85
Dichloromethane	Sweet, chloroform-like	766.7 – 1148.18	205,000 – 307,000
Ethylbenzene	Aromatic, benzene-like	420.3 – 2802	90 – 600
Toluene	Aromatic, benzene-like	40.6 – 60.9	10,000 – 15,000
Tricholoroethylene	Sweet, chloroform-like	123.6	21,400
Tetrachloroethylene	Sweet, ether-like or chloroform-like	365	50,000
Vinyl chloride	Faintly sweet	27.5 – 55	10,000 – 20,000

In real landfill air samples, sulfur compounds tend to have much higher concentrations than other trace odorants and can drown out their signal at times. However, based on psychological testing, seven primary classes of olfactory stimulants have been found to generate specific responses in separate olfactory cells. These odorant classes are shown in Table 6 with a specific model compound and its odor sensitivity limit.

Table 6. Concentrations of primary odor classes to generate an equal odor intensity. (WEF 1978)

Odor Class	Model Compound	Concentration to Generate Equal Odor Intensity (ppm)
Ethereal	Ethylene dichlor	800
Camphoraceous	1,8-Cineole	10
Musky	Pentadecanlacton	1
Floral	Phenylethylmethyl ethylcarbinol	300
Minty	Methone	6
Pungent	Formic acid	50,000
Putrid	Dimethyl disulfide	0.1

In the field, one odorant may dominate over another (at least periodically), or several different odorants may be perceived simultaneously or synergistically but interpreted as an individual unpleasant smell. Table 7 lists the common odor categories used in describing landfill odors.

Table 7. Landfill odor categories and descriptors, ranked in order of most commonly occurring (Decottignies et al. 2009; Curren 2012)

Odor Character Category	Common Descriptors
Non-descriptive	Trash
Sulfur/Cabbage/Garlic	Rotten egg, natural gas, skunk
Rancid	Sour, dirty diaper, sweet-sour
Fecal/Sewery	Feces, manure, sewage
Fragrant/Fruity	Perfume
Solvent/Hydrocarbon	Chemical
Burnt	Burnt rubber, exhaust, burnt trash
Putrid/Dead Animal	Dead animal
Earthy/Musty/Grassy	Musty, decaying vegetation
Sweet	Sweet trash
Fishy/Ammonia	Ammonia

Another useful tool in helping personnel to categorize odors is the odor wheel (Mendrey 2014). The main idea of the odor wheel is to describe more specific odors, and not just broad categories, such as "putrid" or "sweet." Once categorized by the descriptor, odors can be further categorized by odor strength, on a scale from 0-5 or "undetectable to unbearable," or recognize if there is a presence of multiple odors at the site. One example of modified landfill odor wheel is presented is presented in Figure 1.

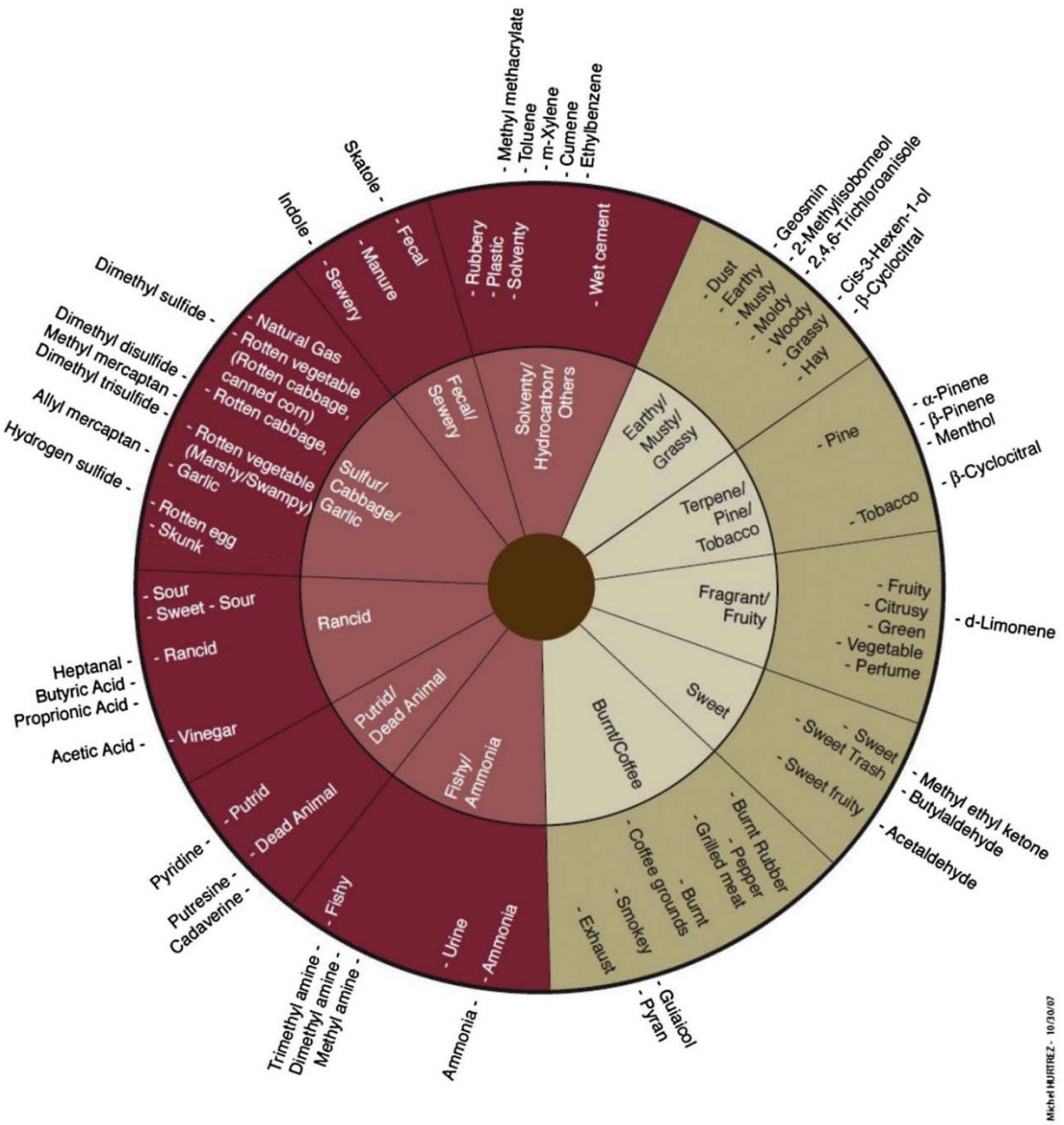

Figure 1. Example of a nuisance odor wheel developed for transfer stations (Curren et al. 2016)

Odors generated at solid waste facilities do not necessarily pose a risk for human health, but they create a nuisance for people living or working near a facility, which could lead to odor complaints (ATSDR 2016) and troubled relationships between the public and landfill management.

1.4 FACTORS INFLUENCING THE DISPERSION OF ODORS

The main factors affecting the dispersion of odors and their potential impact on sensitive receptors are climate, microclimate and topography. Microclimate is the climate affected by the local conditions surrounding the landfill site. Topography is also an important factor affecting odor dispersion since potential sources located at higher elevations than the sensitive receptors are less apt to affect receptors because odors tend to mix and disperse in the air layers above the receptors. However, under certain meteorological conditions, odors generated at higher

elevations can be carried into lower elevations (Epstein 2011). Complex meteorological conditions with highly localized variability makes it hard to predict, much less control, dispersion of odors off-site, while increasing the potential of becoming an odor annoyance to people living and working near the landfill site.

Nevertheless, there seems to be an empirical relationship between some meteorological conditions and the frequency of odor complaints (Blumberg et al. 2001; Epstein 2011; Capelli et al. 2008). For instance, odor complaints tend to occur with no or very weak winds, high humidity, cloudy skies, and in situations where thermal inversions occur (Epstein 2011). Inversion layers tend to trap odors and keep them closer to the ground. These conditions mostly appear early in the morning since there is a higher possibility for stable atmospheric conditions, when there is less mixing of the atmosphere. During unstable weather conditions, such as windy days, clear skies and high solar radiation, the atmosphere mixes more and odor complaint frequency tends to be lower (Energy and Environmental Affairs 2017). With an increase in temperature, particularly early in the morning, odors are more likely to migrate off-site, since higher temperature stimulates faster molecular movement and hence more odor diffusion (Epstein 2011). Even though high temperatures in summer months stimulate increasing strength of nuisance odors, odor emissions have a tendency to disperse more quickly due to successive events of unstable weather conditions. On the contrary, during the winter months, there are less odor emissions due to lower temperatures as well as lower odor dispersion nearer to the source that is affected by more frequent stable atmospheric conditions (Sattler and Devanathan 2012).

High humidity, like high temperature, also influences the strength of odors (Che et al. 2017) because humid air traps odorant molecules and allows them to linger longer than normal. Also, with higher humidity, the human sense of smell is enhanced, since the humid air brings aqueous odor molecules directly to our nose receptors (Kuehn et al. 2007). Similarly, pressure seems to have a noticeable effect as well. Low pressure days appear when there is rain and cloudy skies. When the vapor pressure inside the landfill body is higher than in the ambient air, more landfill gas will escape. The reason for that is that vapors attempt to equilibrate with the atmospheric pressure by migrating from regions of high pressure to low pressure (Wenjing et al. 2015). Precipitation also has a strong impact on both the strength of odors and also how quickly they dissipate. The rate of waste decomposition is affected by the amount of moisture available, which results in higher gas production rates (ATSDR 2017). Rainfall and moisture that collects in the pore spaces in the landfill body force gases to migrate out of the landfill into the ambient air. Conversely, surface soil or cover material that is wet can inhibit the escape of odor gases from the landfill body (ATSDR 2017). A summary of meteorological conditions and their impact on odors is presented in Table 8.

Table 8. Summary of Common Meteorological Conditions and their Impact on Odors

Factor	Conditions	Impact	Reference
Wind speed and direction	• Weak wind, stable conditions • Clear, strong wind, low variability in wind direction	• Highest odor detection • Significantly lower odor detection	(Capelli et al. 2008; Air Quality Management District 2009; SCS Engineers 2009; Baltrėnas et al. 2012)
Temperature	High	• Higher odor detection • Unstable conditions	(USEPA 2000; Sattler 2007; Golder Associates Inc. 2010)
Precipitation	High	• Wet soil prevents LFG migration • Rain seepage into the pore spaces pushes out gases into the atmosphere	(Sadowska-Rociek et al. 2009; Golder Associates Inc. 2010; ATSDR 2017)
Humidity	High or foggy	• Higher odor detection • Warm humid air enhances human sense of smell • Traps smells so they linger longer	(Berglund 1998; Kuehn et al. 2008; Golder Associates Inc. 2010; Che et al. 2013)
Weather conditions	• Clear sky, sunny and windy • Overcast, no wind, high humidity/fog, thermal inversions	• Complaints rarely received • Complaints are more common	(MassDEP, 2007; Air Quality Management District, 2009; Golder Associates Inc., 2010; Epstein, 2011)
Thermal inversions	Season changes (Fall → Winter, Winter→Spring)	During the period of the year in which inversions are more common, odors are held more closely to the ground and are more likely to be detected	(NSWMA 2008; SCS Engineers 2009; Golder Associates Inc. 2010; Epstein 2011; Energy and Environmental Affairs 2016;)
Pressure	Low	More LFG seeps into the air	(USEPA 2000; Golder Associates Inc. 2010; Thompson 2016)

In terms of meteorological factors, investigators have most frequently attempted to correlate wind speed and direction directly to the dispersion of odor emissions and to the locations where citizen odor complaints are received from (Gallego et al. 2008; Sadowska-Rociek et al. 2009; Sakawi, Jaafar, and Mahmud 2011; Baltrėnas et al. 2012). In a study conducted in Lithuania, Baltrėnas et al. (2012) took samples downwind, upwind, and crosswind, from different distances, where the prevailing winds were south and northwest. Odor concentration was expressed in European odor units per cubic meter of air (OUE/m^3), which represents the number of dilutions necessary to make the sample concentration equivalent to the concentration of smell (Baltrėnas

et al. 2012). Results showed that wind direction and wind speed were the major factors influencing the dispersion of odors and the increase in detection concentrations. Higher odor concentrations were noticed when there was a favorable wind direction (SW), compared to lower odor concentrations when not downwind (NE). When winds were 9 m/s from the southwest, the measured odor concentrations were 51 and 61 OUE/m^3 (sampling points 1 and 2), while when the winds were recorded out of the northwest at 2 m/s, the highest measured concentration was nearly 9 times lower at 7 OUE/m^3 (sampling point 4).

In France and Poland (Sadowska-Rociek et al. 2009), an odor survey attempted to correlate the following meteorological conditions to odorant concentrations: air temperature, wind speed, wind direction, atmospheric pressure, precipitation and humidity. However, the results obtained did not show a significant correlation between odorant concentrations and atmospheric conditions due to the small amount of data collected. To test the factors that impact the increase in odor concentrations, a longer study period was performed. It was observed that concentrations of tested odorants were strongly influenced by the wind speed and pressure. On days where the wind speed was high (>25 mph), odor concentrations had a tendency to decrease, while pressure drop caused an increase in the concentrations. With higher pressure (>980 hPa), the concentrations were very low (<100 µg/m^3), as shown in Figure 2. Also, the impact of precipitation was observed on the VOC concentrations in the atmosphere. Events corresponding to precipitation or high humidity frequently resulted in a decrease in VOC concentrations. Generally, concentrations of odor causing compounds decreased on rainy days with strong winds (Sadowska-Rociek et al. 2009).

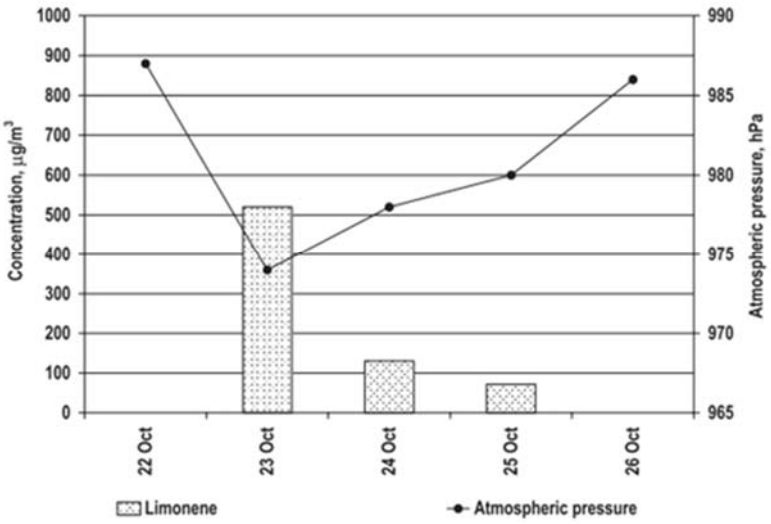

Figure 2. Concentration of Limonene Affected by Atmospheric Pressure (Sadowska-Rociek et al. 2009)

Temperature and humidity are expected to enhance odor perception and how quickly the odors dissipate because they both increase molecular volatility. This is why odors smell stronger in the heat, and cars smell musty after rain. A substance's solubility also affects its odor. Chemicals that dissolve readily in water or fat are usually intense odorants (Detection of Odorants 2016). Higher temperatures in summer produce greater emissions from liquid area sources because of

increased compound volatility; however, these emissions tend to disperse more readily because of frequent occurrence of unstable atmospheric conditions that promote dispersion and mixing. An opposite scenario occurs in winter, with lesser emissions due to lower temperatures, but also frequently less dispersion, due to more stable atmospheric conditions. When the temperature drops, gaseous molecules become denser. Humid air traps odors and causes them to linger longer than they usually would (USEPA 2000).

1.5 ODOR COMPLAINTS

Citizen odor complaints are more frequent in urban areas where people are living and working in close proximity to solid waste facilities (Sakawi et al. 2011; Ying et al. 2012). Due to planned zoning, usually there are other industrial facilities operating close to each other, such that it can be difficult to accurately identify the origin of odors and the responsible party for generating the odor complaints off-site (Sarkar, Hobbs, and Longhurst 2003). Solid waste facilities use odor complaint logs to evaluate their operational performance with regard to nuisance odor emissions. However, odor complaints by themselves cannot be used as a measure to prevent odor emissions since they do not provide true objective, quantitative data on how to minimize the odors nor do they provide any insight on odor migration mechanisms or possible causes. The reason for that is because odor complaint logs often lack valuable information that could potentially lead to better understanding of site-specific characteristics (McKendry et al. 2002; Air Quality Management District 2009; SCS Engineers 2009; Golder Associates Inc. 2010). They can be vague, uncertain and inconsistent with the information given. For example, there is a difference between the exact time when the odor was observed compared to the time when the complaint was filed. Not knowing the exact time of the odor occurrence prevents the possibility of cross-comparison with local meteorological conditions and site activities to accurately identify the source of odor (McKendry, Looney and McKenzie 2002).

Feedback from people living close to a landfill site about the landfill operations, including odors, should be handled effectively, since that is a crucial part of successful management of waste operations (McKendry et al. 2002). Standard ways that citizens submit odor complaints are to the local authorities, regulatory agencies, or directly to the facility. Procedures for odor complaints at a site usually consist of a 24 hour per day phone hotline that goes to an answering service that takes basic information, such as the nature of the event, contact information, when the event started, the time of the call, etc. The call is then forwarded to the responsible site personnel for a follow-up call the next day and courtesy visit to check on the validity of the odor complaint. During the courtesy visit, the trained representative performs an odor survey to verify the odor complaint and suggest corrective action, if warranted. However, what to sample for remains elusive. When correlating information obtained from complaint logs with the actual observations made by solid waste management personnel from the site, at the time of the odor complaint, odor mitigation strategies can be developed to reduce nuisance odor emissions (McKendry et al. 2002; Golder Associates Inc. 2010). Furthermore, a weather station can be installed at the landfill site, which provides real-time information on local meteorological conditions (SCS Engineers 2009). Correlation of meteorological conditions with respect to locations from which odor annoyances are occurring could help in identifying odor sources at the site. Once the source of odor is known, proper monitoring and management of solid waste operations can be implemented with the aim of reducing dispersion to residential areas. For example, by knowing the wind direction, waste can be disposed to an alternate working face, since an odor event will impact residential areas only if favorable wind conditions exist. If the direction of the wind is not towards the working face, or if

the wind speed is too strong or too weak, there will be no impact and thus no change needed to landfill operations (McKendry et al. 2002).

Sakawi et al. (2011) used information on odor perception from 190 surveys collected within a 2 km (1.24 miles) radius of a landfill fence in Malaysia. The results showed that 55% of those surveyed made at least one official complaint to landfill personnel regarding nuisance odors. Those that did not complain, either did not know where to make the complaint, did not care about the odors, or thought that somebody else would file the complaint such that they did not have to. Based on the time of day, the highest detection of odors was at night with 31%, followed by 28.4% who stated that they could detect the odors throughout the whole day. When taking the weather conditions (such as wind direction, wind speed, temperature and humidity) into consideration, 92.6% of respondents stated that they believed that the nuisance odors close to their homes were associated with the weather. Factors such as wind, rainfall and high temperature were identified by 40.6% of respondents as being likely responsible for higher nuisance and odor detection. The most important influence was recognized as wind direction with 30.5%, followed by rainfall with 22.6% and hot weather with 6.3% (Figure 3).

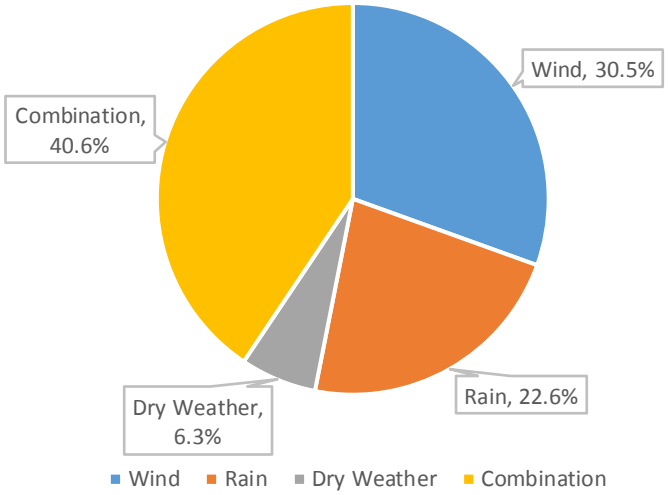

Figure 3. Survey Results of How Weather Conditions Influence Odor Detection for A Neighborhood in Malaysia (Sakawi, Jaafar and Mahmud 2011)

Also, the location of where the odors were initially detected was also asked as part of the survey. The choices were: 1) inside of the house, 2) just outside of the house, and 3) outdoors (such as park, roads, etc.). The worst odors were detected just outside of the house with 50.5%. Based on the perceived odor intensity (Likert scale range from 1-4, where 4 is a strong odor and 1 is barely detectable), 74.2% detected strong odor, as presented in Figure 4 (Sakawi, Jaafar and Mahmud 2011).

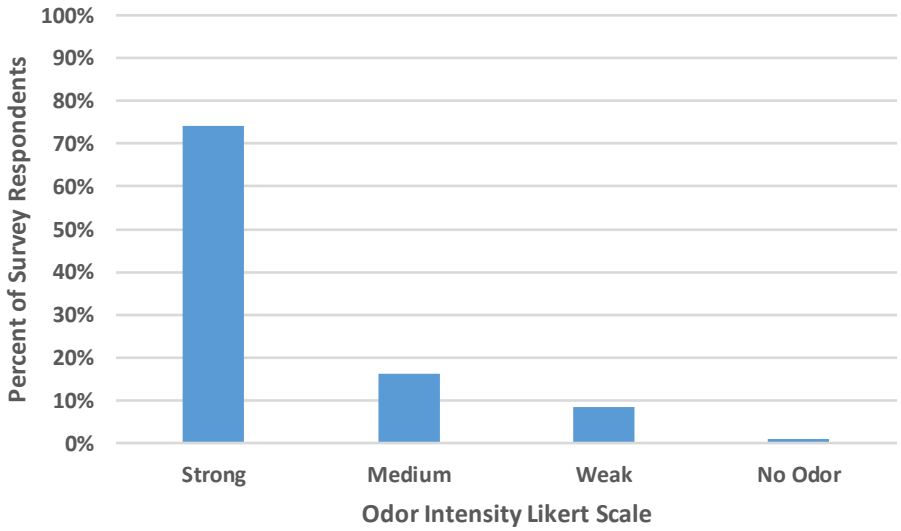

Figure 4. Odor Intensity Recognized by the Respondents of an Odor Survey in Malaysia (Sakawi, Jaafar, & Mahmud, 2011)

Chemel et al. (2011), in France, used odor complaints data coupled with meteorological conditions to identify which weather conditions can be expected to correlate with nuisance odors. The Advanced Research Core of the Weather Research and Forecasting (WRF) model was used for both winter and summer season variations to forecast the scenarios that could cause an increase in the number of odor complaints by the communities located in close proximity to the landfill. Meteorological data (for the period from 2002-2004) on pressure, temperature, humidity, wind speed, wind direction and precipitation was collected from the weather station located at the landfill site. For the same time period, odor complaint data (which included the date, location and duration of the odor nuisance) was acquired (n = 71) from within a 5 km (3.10 miles) radius around the landfill site. The results showed that two types of weather conditions, moderately stable and unstable, triggered the majority of odor complaints, with more than 15 complaints per 100 days, while stable conditions generated less than 7 complaints per 100 days. Wind speed and precipitation were the most descriptive meteorological parameters since precipitation rinses the atmosphere thereby reducing odor concentrations, while wind speed dictates the direction in which odors will be dispersed (Table 9).

Table 9. Weather Classes and Number of Odor Complaints for a study in France (Chemel, Riesenmey, Batton-Hubert and Vaillant 2012)

Regional Atmospheric Stability	Risk of Precipitation	Wind Speed/ Direction		Number of Days	Number of Complaints (*)	Complaints per 100 Days
		>1500 hPa	<1500 hPa			
Moderately stable	Very low	Very low /NA	Very low /NA	121	19 (2)	15.7
Unstable	Very low	Very low /NA	Very low /NA	89	14 (1)	15.7
Neutral	Low	Very low /NA	Very low /NA	182	12 (7)	6.6
Very stable	Low	Very low /NA	Very low /NA	113	7 (2)	6.2

Regional Atmospheric Stability	Risk of Precipitation	Wind Speed/ Direction		Number of Days	Number of Complaints (*)	Complaints per 100 Days
		>1500 hPa	<1500 hPa			
Very stable	Moderate	Moderate /N	Moderate /S	105	5 (0)	4.8
Moderately stable	Moderate	Moderate /E	Moderate /NW	77	3 (2)	3.9
Moderately stable	High	Strong /N	Low /NA	104	4 (2)	3.8
Moderately stable	High	Moderate /S-SE	Moderate /N-NW	82	3 (1)	3.7
Moderately stable	Moderate	Moderate /S	Low /NA	72	2 (0)	2.8
Moderately stable	Moderate	Strong /E	Low /NA	81	2 (0)	2.5
Very stable	Moderate	Low /N	Low /NA	44	0 (0)	0.0

(*) The number of complaints that were identified as being related to special manipulations of waste (e.g. opening of a new cell) is indicated in parenthesis.

With little or no wind, odors tend to be retained longer resulting in higher localized concentrations. The study determined that clear skies and unstable weather conditions contribute the most to odor annoyances; however, the complexity of local terrain should also be considered, since it can affect the meteorological conditions (Chemel et al. 2012).

Che et al. (2013), in China, conducted an analysis of meteorological conditions at different distances from a landfill site with the aim of identifying scenarios that lead to more odor complaints from nearby neighborhoods. Meteorological data was collected for the calendar year of 2011, and the surrounding population was surveyed (n = 845 responses). The results showed that 87.4% of respondents that made odor complaints in that year claimed that the strongest odors tended to occur mostly during summer, while other seasons had substantially lower percentages (spring 5.96%, autumn 4.04%, and winter 2.55%). Summer peak complaints were attributed to impacts of high temperature, humidity and pressure. The average number of odor annoyances in the summer period was 11. In the study area, high temperatures, for the summer month of July, were in the range from 31°C to 37°C (88°F – 99°F), and humidity was in the range of 60-75% due to subtropical high pressures. Generally, those meteorological conditions with low pressure, high temperature and high humidity tend to coincide with an increase in odor emissions (Capelli et al. 2008). Also, it was observed that the winds from the east and southeast were directly correlated to the highest incidence rate of odor complaints. Correlation between the distance from the landfill and the number of odor complaints showed that as the distance from the landfill site increases, the odor complaints decrease since odors cannot be detected in the same concentrations as in close proximity to the landfill (100% of respondents living within 1.86 miles from the landfill noticed nuisance odors), as presented in Figure 5.

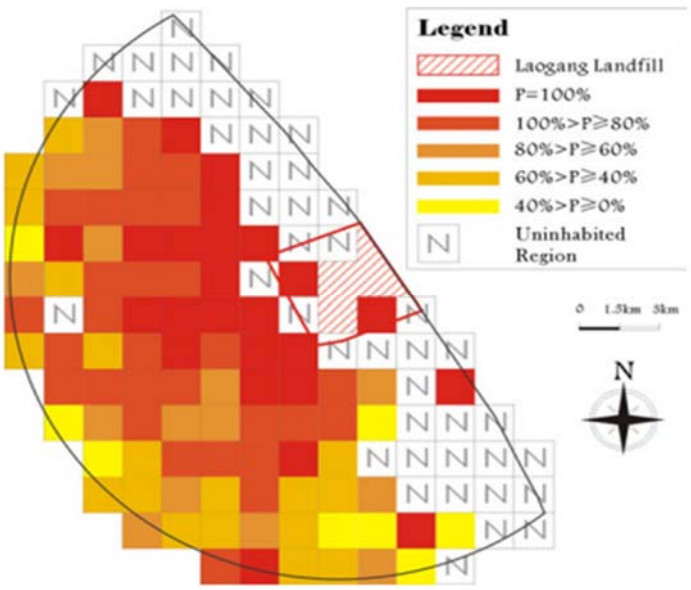

Figure 5. Odor Complaints Correlated to Seasonal Conditions and Proximity to a Landfill Site in China (Che et al. 2017)

Figure 6 shows that the majority of odor complaints was received from the communities surrounding the landfill that were directly downwind in the northwest quadrant (Che et al. 2017).

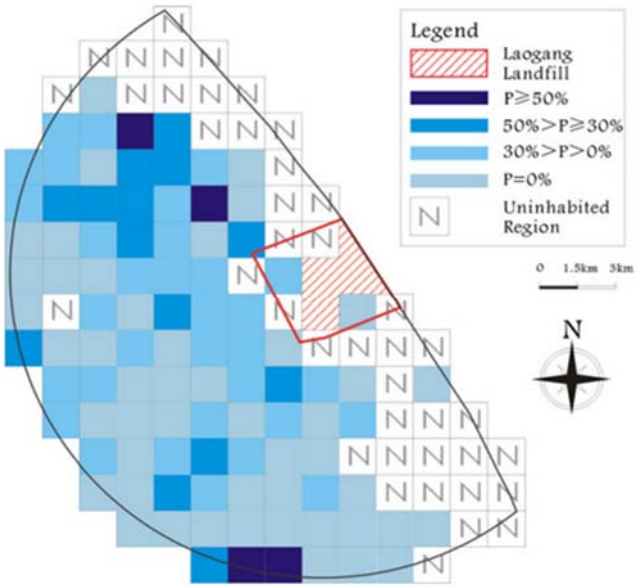

Figure 6. Odor Complaints Correlated to Distances from a Landfill Site in China (Che, Yang, Jin, & Zhang, 2017)

In summary, certain meteorological conditions such as temperature, humidity and pressure are known to influence the emissions of odors, while wind speed and wind direction are responsible for dispersion of odors downwind to residential areas (Ying et al. 2012). Odor causing compounds

can be dispersed for a distance of a mile or more from the source in the landfill site (Qdais 2007) Establishing appropriate procedures for dealing with odor complaints while including the most accurate information on the weather conditions will allow landfill managers to correlate citizen odor complaints, meteorological parameters, solid waste operations and other activities that generate odors such that operations can be delayed to when weather conditions are less probable to generate off-site odors, for example.

1.6 ODOR DETECTION TECHNIQUES

Proper characterization and measurement of odors are crucial components of detection. Some of the challenges in odor detection are related to the chemical complexity of odorous gas emissions and the subjective character of the human sense of smell in odor perception (Lebrero et al. 2011). State of the art analytical measurements that characterize specific odorants in terms of their chemical composition and concentration are objective, repeatable, and accurate; however, they provide little information about odor perception by human receptors (Lebrero et al. 2011), and they can only detect individual known odorant compounds. Hypothetically, the odor contribution of landfills should be measured by identifying, sampling, and quantifying the concentrations of all odorants from all odor sources. But this is extremely difficult and expensive to accomplish due to the nature of the wide variety of compounds known to cause odors in landfills (Paxeus 2000; Bruno et al. 2007; Kjeldsen 2010).

Current approaches to odor measurement and regulation vary among local jurisdictions, states, and countries. However, the key breakthroughs in odor characterization have occurred during the last 15 years with the development of capillary chromatography and solid phase microextraction techniques, gold film H_2S sensors, and the standardization of olfactometry (Hobbs 2001; Van Harreveld 2004). Regulatory tools have ranged from relatively simple qualitative measurements of odor and/or specific chemicals to the more complex use of electronic nose technology and atmospheric dispersion models to predict odor impacts on neighboring receptors. The most common techniques for odor detection are: 1) dynamic dilution olfactometry, 2) chemical analyses, and 3) electronic nose technology (Capelli et al. 2013).

Odor detection techniques are mainly focused on sensory analysis where the human olfactory sense has the ability to detect the existence of some odor causing compounds in the ambient air. The reason for that lies in the fact that many of the chemical detectors are not as responsive for the odor causing compounds when compared to the human nose (Van Ruth 2001). Odors recognized by a human's sense of smell can serve as an early warning signal of gas emissions from a landfill site. A common approach for measuring odor concentrations is dynamic dilution olfactometry based on the human perception of smell. In this method, a trained panel of odor experts is exposed to a sample of odorous air in different dilutions to determine the threshold of the odorous emissions (St. Croix Sensory 2005). In the beginning, the degree of dilution is very high, such that most of the trained panelists will not observe the odor. Then, the sample is diluted less and less, and this process continues until all the panelists perceive the odor and confirm that they smell it (Baltrėnas et al. 2012). Since human responses to odor can be subjective and vary among individuals, multiple panelists with tested sensitivities within a controlled range are required to reduce the uncertainties. In practice, a team of panelists is reduced to just two, and sometimes to only one (Nicolas et al. 2006). Both field and laboratory olfactometry measurements have been used to quantify odors at different magnitudes. However, these techniques are expensive, subjective, or largely inaccurate and not reproducible.

Current research (Liu et al. 2013; Sakaran et al. 2012) has focused on interpreting the presence/absence of odors at extremely low detection limits with rapid response times. However, these techniques are irreversible, odorant-specific, and non-quantitative. Carlson et al. (2006) were able to synthesize a chemical sensor specific for fluorene with a detection limit of 10 parts per trillion, using molecular imprinting technology. However, follow-up experiments with structurally similar odorants such as naphthalene, anthracene, and fluoranthene showed that binding is highly selective for fluorene only and is irreversible. The authors suggested that the reversibility of the sensor signal can be improved by modifying the binding site, but that would require modifications for each and every specific odorant molecule, limiting its application. Liu et al. (2013) developed an agarose-gel supported film coated with quinine sulfate with a pH-dependent spectrophotometric response to organic acids such as isovalric acid, hexanoic acid, and octanoic acid (components of body odor) to detect presence/absence, but no way to quantify the signal was suggested.

Chemical analyses, on the contrary, are more objective, precise and repeatable in quantifying specific odorants (Lebrero et al. 2011). Techniques such as gas chromatography coupled with various detectors or mass spectrometry (GC/MS), are used for the characterization of the chemical composition of odorous gas samples (Smet et al. 1999). As an analytical measurement, it allows detection of odor causing compounds with low odor thresholds that can be categorized as a source of nuisance odors. Even though results can show a wide range of compounds present in the sample, analytical methods for every single odorant are not developed as yet and the methods cannot show how actually certain odorants are perceived by the human sense of smell. Also, it cannot be directly correlated with an odor characterization (Göpel 1998). Dincer et al. (2006), in Turkey, investigated the composition of odorous gasses generated at a landfill site using GC/MS. Detected VOCs consisted of sulfur/nitrogen compounds, monoaromatics, aldehydes, esters, halogenated compounds, ketones, and volatile fatty acids. The highest concentrations identified were monoaromatics (47.4 $\mu g/m^3$) and halogenated compounds (62.9 $\mu g/m^3$). Two sampling periods were selected, May and September, with five sampling points. In both periods, the total VOC concentrations were very similar except for sampling point 5 (Figure 11). The reason for that was ongoing waste burial in May, while the site was covered with soil during September.

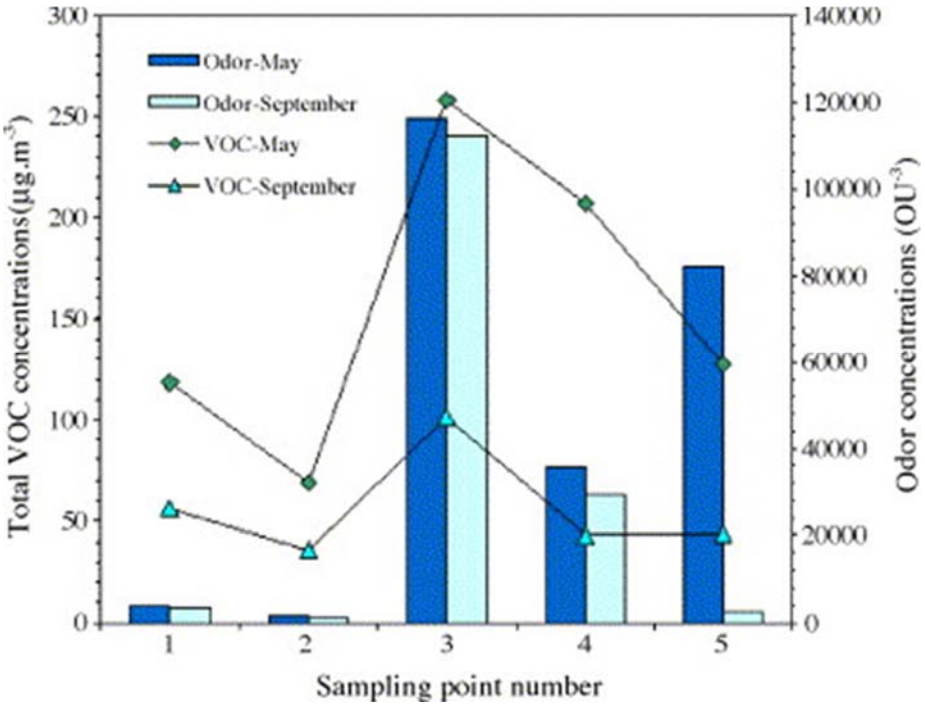

Figure 7. Relationship between Odors and Total VOCs Concentrations, in May and September for a Landfill in Turkey (Dincer et al. 2006)

Statistical analyses were performed to determine a correlation between chemical concentration and odors (Table 10) with the most correlated groups highlighted in bold. Aldehydes, ketones and total VOCs were compounds identified as the best estimators, with $r^2 = 0.96$ (n=10, p<0.01) (Dincer et al. 2006).

Table 10. Pearson correlation coefficients between the different compound groups and odor (n = 10) (Dincer et al. 2006)

Parameter	Odor	Total VOCs	Acids	Aldehydes	Esters	Halogenated compounds	Monoaromatics	Ketones	S and N compounds
Odor	1	**0.64***	0.23	**0.91***	0.52	−0.10	0.55	**0.73***	0.41
Total VOCs		1	0.63	0.76*	0.87*	0.23	0.93*	0.88*	0.02
Acids			1	0.21	0.61	−0.18	0.69*	0.37	−0.33
Aldehydes				1	0.58	−0.04	0.66*	0.91*	0.53
Esters					1	0.02	0.94*	0.79*	−0.30
Halogenated compounds						1	−0.03	−0.02	−0.03
Monoaromatics							1	0.83*	−0.18
Ketones								1	0.29
S and N compounds									1

*Statistically Significant (P<0.05)

While measuring odors by using a trained panel followed by GC/MS is valuable, it is also time-consuming and resource intensive, which is why these types of measurements are rarely carried out in practice (Nagle et al. 1998). A more rapid way of monitoring odors, in the field over

different time periods, is performed using an electronic nose, which is a sensor array capable of mimicking the behavior of the human olfactory system to identify and distinguish between different odor causing compounds, gases and vapors (Bhandare et al. 2013) The key components of an electronic nose are: 1) the observing system, which detects the odors, and 2) the pattern identification system, which uses a set of electronic elements to interpret the signal. The electronic nose can be used to identify odorants, determine their concentrations, and characterize the odor perception (Keller et al. 1995). Using coffee for example, the human sense of smell detects the whole chemical composition as "*coffee*," while electronic noses detect the coffee as a mixture of multiple chemicals acting together to produce the odor of coffee (Blesson et al. 2013). Unfortunately, the system must be calibrated to laboratory olfactometry measurements, which are again limited by human subjectivity.

Capelli et al. (2008) considered the use of different odor detection techniques including chemical analysis, dynamic olfactometry and electronic noses, in estimating the odor emissions migrating off-site from a solid waste facility in Italy. Also, the techniques were compared to see if a correlation could be demonstrated. Four seasonal periods of monitoring were used: winter, spring, summer and fall. Examined pollutant compounds found at the waste grinder were linked to theoretical odor concentration values. Results showed that chemical analysis by GC/MS can be a useful tool for identifying chemical composition of odorous sample while there was no obvious correlation between the results obtained by chemical analysis and olfactometric analysis (Figure 8). The reason for that lies in the fact that the human sense of smell cannot distinguish all of the individual components present in an odorous sample and instead detects them as a whole, which results in a high level of inaccuracy.

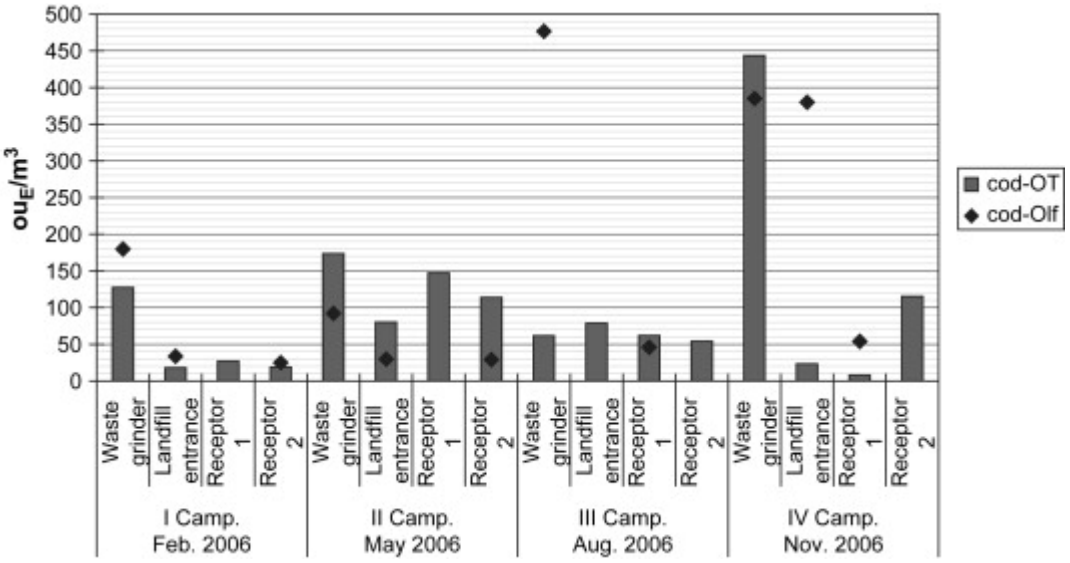

Figure 8. Comparison Between Odor Detection Concentration Values Measured by Olfactometry (cod-Olf) and Theoretical Odor Concentration Values (cod-OT) (Capelli et al. 2008)

Ambient air monitoring with the electronic nose technology showed the time percentages in which the instrument perceived the presence of odors from the landfill (Figure 9). A possible correlation between the results acquired by electronic nose and by dynamic olfactometry was

found. This was not unexpected because they were both calibrated based on the same human panel. However, the results revealed that even though three different types of techniques for odor identification do not necessary correlate with each other, they each have value in demonstrating the complexity of odor monitoring (Capelli et al. 2008).

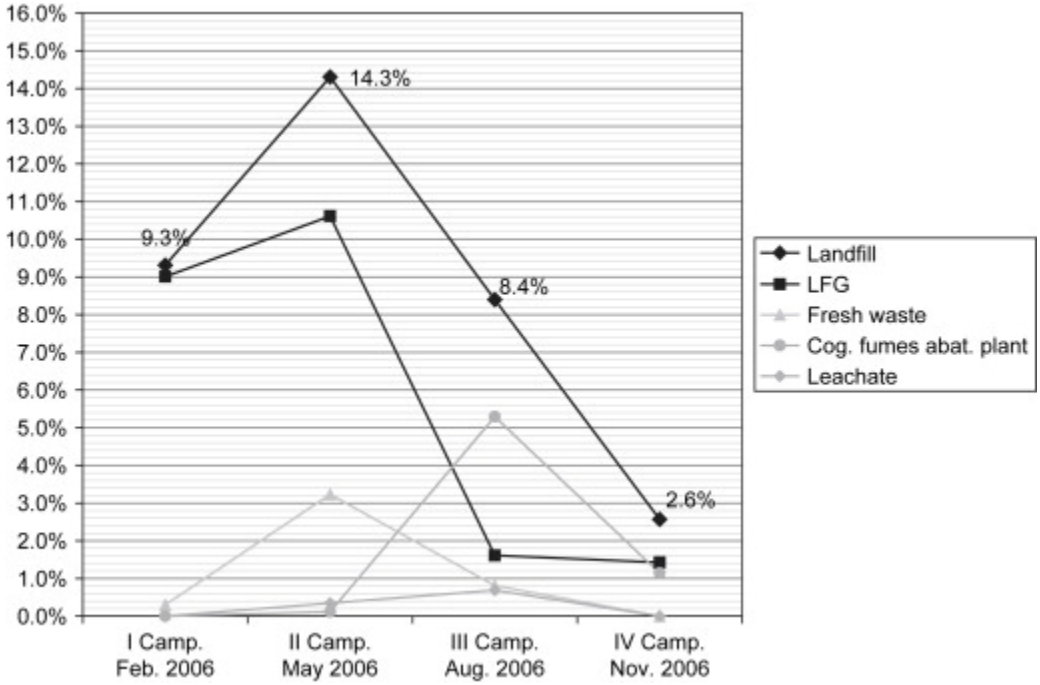

Figure 9. Recognition of Different Olfactory Classes by Electronic Nose at Receptor 1 (Capelli et al. 2008)

Previously, analysis of meteorological conditions showed that higher odor detection was observed during periods of weak wind with random changes of direction, while during strong winds with an established predominant wind direction, odor detection at the same locations was notably lower (Capelli et al. 2008), showing how the monitoring of meteorological conditions can be a useful tool to assess odorant emissions transmitted from a landfill site to nearby neighborhoods. Also, each of the different techniques used for odor detection can be implemented at the same site while obtaining vastly different results. A summary of advantages and disadvantages of each of the major odor detection techniques in presented in Table 11.

Table 11. Advantages and Disadvantages of Various Odor Detection Techniques

Technique	Type	Method	Advantages	Disadvantages	Reference
Chemical Analysis	Analytical	GC/MS	• Detection of pollutants with low odor detection • Useful to analyze odor composition • More objective, repeatable and accurate	• Difficulty in relating the chemical composition of an odor mixture to its olfactory properties • Little information about the odorant real impact on human receptors	• Capelli et al. 2008 • Bratolli et al. 2011 • Lebrero et al. 2011 • Capelli et al. 2013 • Capelli, et al. 2014
Dynamic Olfactometry	Sensorial	Human nose as a sensor	• Most common approach • Determine the odor concentrations	• Subjective • Expensive ($224-$336 per measurement) • Time consuming	• Capelli et al. 2008; • Lebrero et al. 2011 • Baltrėnas et al. 2012 • Gutiérrez et al. 2015 • Deshmukh et al. 2017
Electronic Noses	Senso-Instrumental	Artificial noses, which can distinguish between different odors Single odorants, such as H_2S and NH_3, have been commonly used as surrogate markers	• Make assumptions about the landfill odor impact on the points where instruments are installed; • Useful management tool (for both laboratory and on field purpose)	• Dependent upon operational choices • Only partial characterization of odor emissions • Problems with reliability and sensitivity, especially to temperature and humidity	• Capelli et al. 2008; • Lebrero et al. 2011; • Capelli et al. 2013; • Capelli et al. 2014 • Deshmukh et al. 2015 • Giungato et al. 2015 • Giungato et al. 2016 • Eusebio et al. 2016

Atmospheric dispersion models have also been used to predict odor impacts on downwind receptors. However, inputs to these dispersion models include odor concentrations estimated using subjective olfactometry or electronic nose measurements. Furthermore, dispersion models

merely predict the number of dilutions needed to reach a perception threshold at a certain distance from the emission source. Such predictions cannot entirely predict odor annoyance unless the relationships between odor concentration and perceived intensity and offensiveness can ever be determined with certainty (Laor et al. 2014). Furthermore, they also suffer from being largely irreversible, odorant-specific, and non-quantitative (meaning they must be calibrated using subjective methods).

1.7 ODOR MANAGEMENT TECHNOLOGIES

Testing different sources at the site can provide information on concentrations and emission rates to determine the magnitude of an odor problem (Kehoe et al. 1996). This information could be useful for implementing proactive strategies to address migration of odors off-site. If, for example, forecasts of meteorological conditions conducive to odorant transport can be identified in advance, odor emissions can be minimized by altering landfill operations ahead of time (Strech et al. 2001). Once odorant and sources have been identified, the next step is to implement an odor managment strategy.

Some odor management technologies prevent odorants from migrating outside of the landfill site (Epstein 2011), while others are successful in minimizing the impacts. A summary of these include the following:

1) **Cover management**: placement of daily cover on recently unloaded waste while also reducing the odors from gases generated by bacterial decay
2) **LFG flares**: thermal destruction of odor causing compounds in the landfill gas
3) **Process modification**: adjustment of solid waste operations in order to reduce the production of odorous compounds
4) **Biofiltration**: venting of LFG through a biological media filter, resulting in often less offensive odorant release (ATSDR 2001)
5) **Incineration**: oxidation of hydrocarbons and VOCs to carbon dioxide and water vapor, while any noncombustible materials (glass, metals, etc.) remain as ash (Kehoe et al. 1996)
6) **Odor masking**: also referred to as deodorization, refers to superimposing a pleasant odor to neutralize or outcompete the unpleasant odor
7) **Adsorption**: adhesion of odorant molecules to a surface such as activated carbon, catalytic carbon, or other engineered media

In cover management, soil cover is used daily to reduce the intensity of recently placed wastes (ATSDR 2001). More substantial covers are implemented at landfill closure to minimize potential of moisture infiltrating the refuse, encouraging bacterial growth and further decomposition (ATSDR 2001). A study by Anunsen (2007) tested three different types of landfill covers (red soil, wood mulch and compost) to reduce odors from LFG at smaller or older landfill sites. Results revealed that red soil (containing appreciable levels of iron) could be successful in reducing concentrations of H_2S, with the capability to dilute H_2S at a LFG flow rate of 100 Lpd/m^2 with H_2S concentrations of 40 ppm to 40 Lpd/m^2 at 10 ppm (Anunsen 2007).

Flaring is a combustion technology used to destroy the compounds in LFG with a destruction efficiency greater than 98% (ATSDR 2001; Caulton et al. 2014). It is most efficient if the LFG is composed of at least 20% methane by volume to avoid supplemental fuel costs to operate the flares (ATSDR 2001). In addition to producing methane and carbon dioxide, anaerobic processes

also generate H_2S and siloxanes. Siloxanes are large molecules that mainly consist of silicon and oxygen. These contaminants become a concern when they volatilize into the LFG and during flaring operations, microcrystalline silica can be created, which can damage gas engines, heat exchangers, etc. It is recommended to clean the LFG before combustion to avoid any operational, health and environmental issues (Ajhar et al. 2010). Efficiency of the process is greatly affected by operational conditions but also relies on other factors, such as: wind speed, gas heat content, and the absence of water or hydrocarbons in the gas flow (Cid-Vazquez et al. 2012).

Process modification is another strategy that includes adjusting the solid waste operations in order to reduce the production of odorous compounds (Strech et al. 2001; McKendry et al. 2002). Those can vary from simple changes in operations to extreme ones, such as the following:

- use more than one working face accessible at any time depending on monitored meteorological conditions
- reduce the size of the active working face
- increase the depth of cover material and/or replace the type of cover material on landfill surfaces
- avoid delivery of highly odorous wastes when the wind direction is unfavorable
- use route control to minimize the contact of waste handling vehicles with residential areas
- record all site activities on a daily basis for possible identification of specific activities that could lead to an odor annoyance

For exhaust streams containing VOCs, biofiltration can also be effective with a reported process removal efficiency of greater than 99.8% (Stanley and Muller 2002). Biofiltration is effectively used to treat a variety of biodegradable, water-soluble contaminants (Harshman and Barnette 2000). This process uses a bed of biologically activated material through which the exhaust stream is fed. Compounds are microbially oxidized by the native bacteriological consortium in the biofilm when the odorants adsorb onto the media. No waste is produced, but there is a need for regular media replacement to avoid clogging or ponding. It has the ability to handle high (>200 ppm) concentrations of H_2S at lower velocities (12-54 fpm) with low maintenance costs in media replacement since the lifetime is usually 3-5 years. However, it cannot remove all odor causing compounds such as those that are not readily biodegradable (Stanley and Muller 2002). Also, the media requires constant moist conditions (USEPA 2000). Biofiltration has relatively low operations and maintenance costs (water use, landscaping control, and periodic media replacement), although it requires a relatively large land footprint and involves energy costs in the form of pumping/aeration (Burgess et al. 2001). Furthermore, ammonia and nitrogen-based compounds are not effectively treated in this manner (Harshman and Barnette 2000), even though nitrogen is a macronutrient.

Incineration is one of the most commonly used odor control technologies. Hydrocarbons are oxidized to carbon dioxide and water vapor while any noncombustible materials (glass, metals, etc.) remain as ash. In situations where odorants are flammable, this process efficiency has been reported as greater than 95% (Kehoe et al. 1996), potentially reducing the weight of waste up to 75% and volume up to 90%. However, there is also an environmental concern due to

contaminant emissions released, such as dioxin and mercury (Dasgupta, 2015), which must be dealt with using additional air pollution control devices.

Masking agents, surfactants and neutralizers are chemical additives that can be administered alone or in combination by air spraying, mixing or surface application. Odor masking introduces pleasant smelling compounds to counteract the nuisance odor impact. However, they do not lower the concentrations of odor causing compounds nor do they minimize the impact of odorants on human health (Choi et al. 2012). Masking agents, such as organic compounds and derivatives from synthetic aromatic chemical manufacture (e.g. vanillin, methyl ionones, eugenols, benzyl acetate, phenylethyl, alcohol, heliotropin) are designed to imitate natural and pleasant odors that are not considered as offensive to the human sense of smell (Von Bergen 2012). Some masking agents contain terpenic compounds that work by blocking or inhibiting specific odor receptors. For example, eucalyptol inhibits ethyl mercaptan receptors, coumarin inhibits skatole receptors, and methyl salicylate inhibits pyridine receptors (Bruchet et al. 2009). Surfactants are amphipathic molecules such as esters like isoamyl acetate, glycols and alcohols that act as emulsifiers between odor molecules and the aqueous solution; that is, they prevent odors from volatilizing by increasing their solubility (Decottignies et al. 2007; Estrada et al. 2013; Vane and Giroux 2000). Neutralizers (odor counteractants) used in solid waste management are typically aliphatic and aromatic aldehydes. They are applied directly to emissions because they structurally modify odorous compounds such as amines, ammonia, hydrogen sulfide and mercaptans, abating their annoyance (Estrada et al. 2013). Although there are many odor neutralizers, masking agents and surfactants on the market, Decottignies et al. (2007) and Bruchet et al. (2009) found that their actual efficiency and mechanisms of action are not well understood. For example, head space injection coupled with GC/MS and sensory analysis similar to olfactometry using human panelists was used on odorant emissions before and after application of one of these masking agents, but no significant difference was found. Additionally, some of the products labeled as neutralizers were actually masking agents. The masking process is greatly affected by geography and topography since effectiveness decreases with distance from the source (Kehoe et al. 1996). Application is simple and requires minimal capital investment related to equipment required for proper operation (Lang et al. 2005); however, chemical replacement costs add up over time. Masking agents should never be used to cover up a toxic concentration since it could be fatal to receptors who do not recognize the danger. Nevertheless, it is the most often applied technology for odor control at sites participating in this study (Personal communication with site personnel). Masking agents are mostly non-toxic compounds that do not pose a threat human health, but sometimes the perfume can also be recognized as a nuisance odor itself (USEPA 2000).

Adsorption processes, such as activated carbon, can also be effective, particularly when the concentration of the pollutants in the airstream is low (Shareefdeen and Singh 2005; Von Bergen 2012), although the efficiency of the process decreases with time, since the adsorbent binds more and more of the odorants, reducing the remaining available surface area for adsorption (Kehoe et al. 1996). Activated carbon adsorption technology is reportedly very effective in removal of odor causing compounds (99%), relying on the fact that it is a relatively simple technology that does not require water use or electricity utilization nor any moving parts or additional pumps (Lang et al. 2005). The technology requires periodic media replacement, which can be costly since the spent carbon must be adequately disposed of or regenerated (Stanley and Muller 2002). The major disadvantage is its inability to effectively remove ammonia or nitrogen-based compounds

(Lang et al. 2005), but for this alternative analysis, the main focus is on removal of sulfur-based compounds.

A summary of the odor management technologies with advantages, disadvantages, removal efficiencies and preliminary costs are presented in Table 12.

Table 12. Advantages and Disadvantages of Currently Available Odor Mitigation Technologies (Sungthong et al. 2011; Bindra et al. 2015; Emam 2015)

Technology	Advantages	Disadvantages	Efficiency (%)	Cost (Capital/ O&M)
Cover Management	• Best management practice • Helps reduce odors from newly deposited waste • Minimal O&M costs	• Not a removal process, only a barrier • Costs vary based on the type of material selected • Limited capacity	>99* 65** 30***	Low/ Low
Flaring	• Can be installed nearly anywhere even with poor LFG quality	• Generates noise and heat • Source of greenhouse gasses emissions • Fire/explosive hazard • Energy value of LFG is wasted	>98	High/ Moderate
Process Modification	• Decreases emissions of odor causing compounds at the source	• Limitations related to waste pick-up and drop-off handling due to traffic conditions • Unpredictable weather conditions • Insufficient land capacity • Increased management activities required	NA	Low/ Moderate
Biofiltration	• Simple technology • No chemicals required • Odor compounds transformed	• Large land area required • High energy demand • Water demand	>90%	Moderate/ Low

Technology	Advantages	Disadvantages	Efficiency (%)	Cost (Capital/ O&M)
Incineration	• Excellent for VOCs • Good for concentrated air streams • Odor compounds are completely oxidized • Small footprint	• Requires air pollution control technologies for air toxics, SO_2 and NO_x emissions • High capital and O&M costs	>95%	Very High/ High
Odor Masking	• Low capital costs • Efficient for intermittent or variable odor events • Small space requirements	• Odor is just masked, not destroyed • Agents can be perceived as nuisance odors • Multiple units needed to cover a large area	0%	None/ Moderate
Adsorption (Activated Carbon)	• No chemicals or pumps • Simple system and minimal O&M • Small space requirements	• Not effective for treating ammonia • Solid waste produced if spent media is not regenerated	99%	Moderate/ Low

***Sandy soil modified with 5% hydrated lime and fine concrete**
****Clayey soil**
*****Sandy soil**

Two primary physical odor mitigation strategies that are cost efficient and control the dispersion of malodorous emissions are buffer zones and turbulence inducing structures. Buffer zones are a minimum distance from the odorous emission source to any residential area such that odor nuisances would be reduced by way of maximum dilution with air. Buffer zones can be established based on odor dispersion modeling. However, meteorological conditions such as humidity, rainfall, atmospheric stability, pressure, wind speed and wind direction have a significant impact on the efficacy of buffer zones, especially if the conditions vary from those under which a buffer zone standard was established. Potentially due to the stripping effect of flooding, rainfall events may promote dispersion of malodorous compounds from open sources such as landfills more than other meteorological parameters (Chemel et al. 2012; Estrada et al. 2013; Lebrero et al. 2011). The other physical mitigation strategy involves turbulence inducing structures such as windbreaks, high barrier fences and tree belts, which disrupt wind currents, thereby decreasing wind speed, increasing dilution/mixing of the odorous emissions, and reducing particulates and dust and other odor carriers. Tree belts are superior to fences since adsorption and absorption on the foliage and subsequent microbial uptake may further assist odor removal, naturally (Hernandez et al. 2012; Lin et al. 2009).

Bortone et al. (2012) evaluated the impact of odor emissions from a landfill site on nearby workers and residents in order to propose management practices for control and minimization of odors dispersing off-site in Italy. Data on weather conditions on an hourly basis was collected and analyzed to see if any patterns in frequency of odor complaints emerged. Three different locations were investigated: 2690 feet (SC-1), 4265 feet (SC-2) and 4921 feet (SC-3) from the landfill site. Results showed that odor emissions do not reach the highly-populated neighborhood (SC-3) furthest from the landfill, while a different scenario occurred for the school (SC-2). From the results presented in the Table 13, it can be observed that the highest value of 3 OUE/m^3 occurred less often than in the closest sampling area to the landfill, yet the 98th percentile concentrations exceeded the 1.5 OUE/m^3 level 200 times, attributed to complex weather conditions and topography, since it has lower elevation than the source of the odor emissions. Also, it was observed that the highest number of exceedances of the 3 OUE/m^3 threshold (n = 73) was recorded for location SC-1, which is closest to the landfill site (Table 13).

Table 13. Thresholds Exceeded in Three Different Locations Near an Italian Landfill (Bortone et al. 2012)

Site	Times 1.5 o.u./m^3 exceeded		Times 3.0 o.u./m^3 exceeded		98th percentile (OUE/m^3)
	n	**%**	***n***	**%**	
SC-1 (2690 ft)	183	2.09	73	0.83	1.71
SC-2 (4265 ft)	200	2.28	41	0.47	1.78
SC-3 (4921 ft)	76	0.87	0	0	0.70

Figure 10 shows the spread of odor intensity in relation to the three different monitored locations. The methodology developed in this study can be helpful in accomplishing successful control, coupled with monitoring of weather conditions (Bortone et al. 2012). Some of the odor control methods proposed were: dealing with the waste disposal as fast as possible during the day, building the cells 13-16 ft high, covering the waste with a clay layer of 1.6 ft deep, keeping the volume of the waste under pressure with a biofilter, and scheduling the spraying of odor masking agents on the surface of the waste.

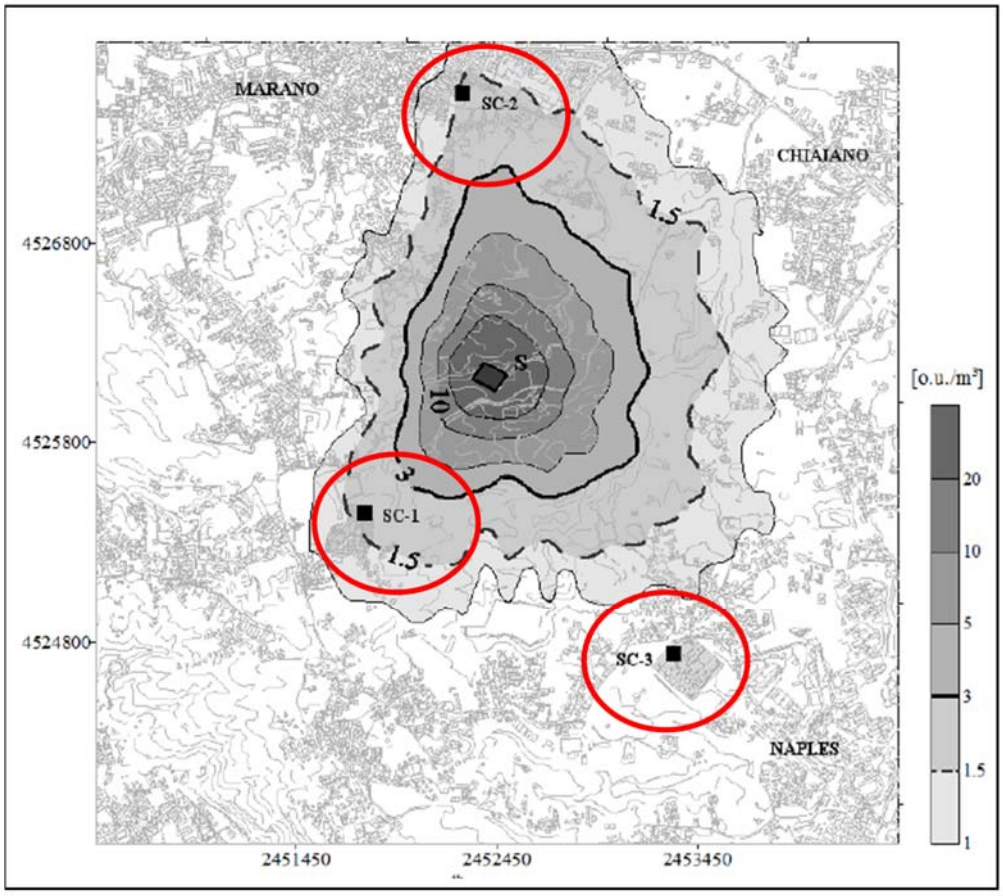

Figure 10. Odor Intensity Curves Near an Italian Landfill (Bortone et al. 2012)

1.8 ODOR SCIENCE

Although the mechanism of how odors are perceived in humans is not fully understood, there are some widely accepted theories of olfaction to draw from. First, humans inhale the air, and approximately 10% of the air containing the odorants will pass under the olfactory organ, the epithelium (refer to Figure 11). Another 20% will pass under the epithelium during sniffing. The epithelium consists of up to 10 – 25 million olfactory cells. The mucus layer on the epithelium traps chemical odorants that are water soluble, and an electrochemical response is created that, depending on its strength, is sent along to the brain in the form of pain stimulus (Epstein 2011).

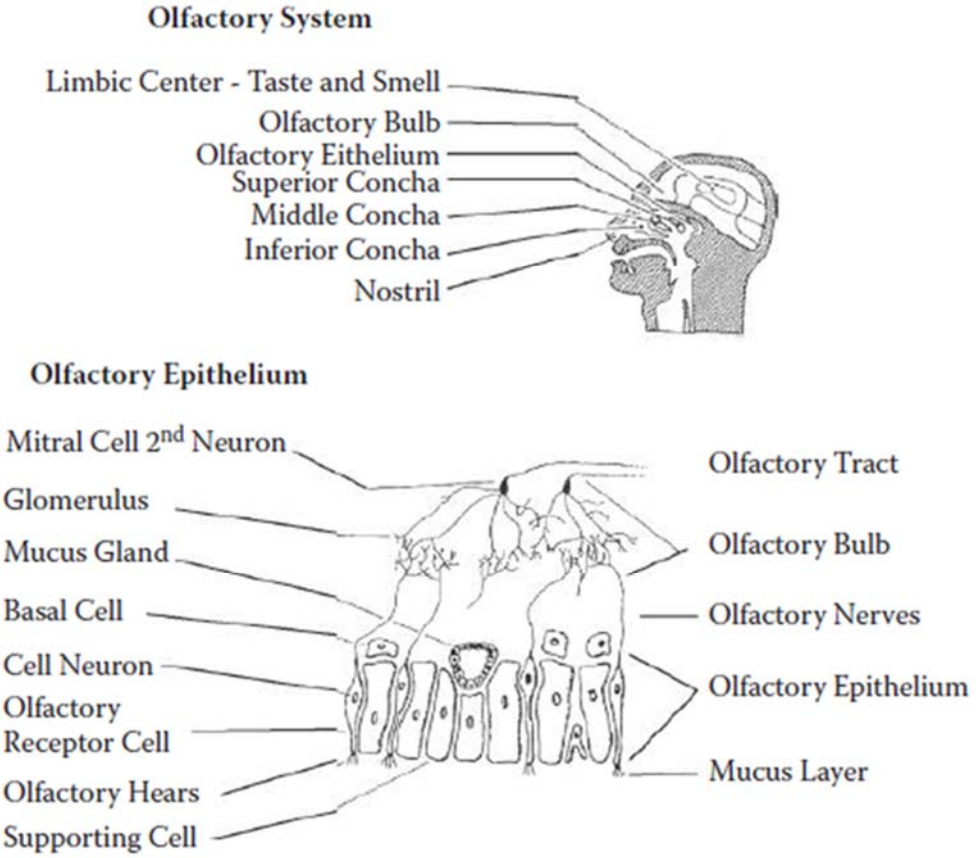

Figure 11. Odorant Receptors and the Organization of the Olfactory Systems (Epstein 2011)

1.8.1 Human Olfaction

Evidence of odorant binding proteins (OBP) in the mucus of the olfactory cleft were reported by Briand et al. (2002). Previously, OBPs were isolated from cow, rat, pig, mouse, rabbit, sheep and porcupine (Ronnett 1995; Briand et al. 2002). These odorant binding proteins account for 1% or more of the soluble nasal proteins and act as carriers of hydrophobic odorant molecules through the 1 to 2 liters of aqueous mucus produced daily by the glands associated with the nasal passages (Ronnett 1995). From the nasal passages, odorants enter into the squamous, transitional and respiratory epitheliums of the nasal cavity. Chronic exposure to toxicants such as ozone and cigarette smoke can cause metaplasia of the transitional epithelium. The odorants then arrive at the olfactory epithelium, classified as neuroepithelium, which is comprised of bipolar primary sensory olfactory neurons, supporting (sustentacular) cells, duct cells of the Bowman's gland and basal cells. During monthly total regeneration of the epithelium, these basal cells, also called adult stem cells, differentiate into supporting cells and 30 million olfactory-receptor neurons, an uncommon process for neuronal cells. The axons of sensory neurons form nerve bundles with other axons, which protrude into the olfactory bulb, making them the only cells in the body that directly contact both the central nervous system and the external environment (Doty 1997). Molecular components within the cell membranes of the sensory neurons convert chemical odorants into a biochemical cascade of signals to the brain (Hatt 2004).

1.8.2 Human Odorant Binding Protein

Odorant binding proteins are present in high concentrations in the aqueous nasal mucosa of humans. They are of the lipocalin superfamily according to their 3-dimensional structure (Figure 12 and Figure 13): a β-barrel with eight strands, and at the C-terminus of the protein, a cavity lined by a short α-helix where binding of hydrophobic molecules, which odorants typically are, occurs (Vincent et al. 2000; Whitson and Whitson 2014).

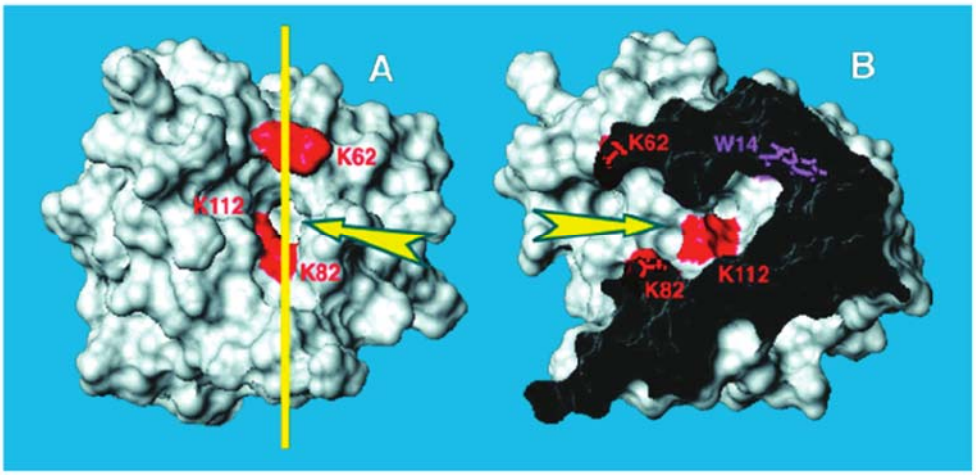

Figure 12. Views of the molecular surface of the predicted tertiary structure of hOBPIIaR. Automated alignment and modeling were performed with the major horse allergen (PDB accession number 1EW3A). (A) Front view of the protein with opening of the binding pocket indicated by an arrow. (B) Rotation of 90° showing a vertical section of the model through the binding pocket, as indicated by a yellow line in panel A. In the binding pocket, lysine side chains and surfaces are colored in red, tryptophan in violet (Briand et al. 2002)

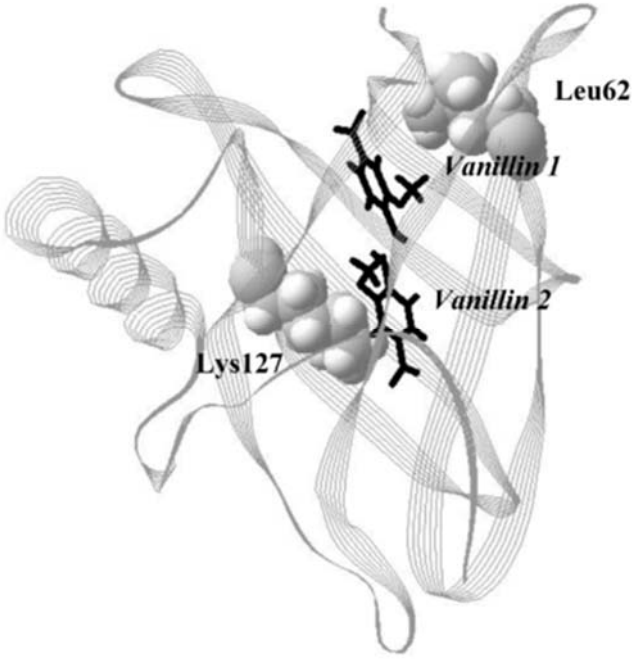

Figure 13. Homology model of hOBPIIa with two ligands in energy minimized positions. Two vanillin molecules (black stick models) can be easily accommodated in the hydrophobic cavity of the beta-barrel. Selected amino acids in close proximity to the docked ligands are in space-filling representation (Whitson and Whitson 2014)

According to Briand et al. (2002), human odorant binding protein (hOBPIIa) is able to bind a diverse array of odorants with a special affinity for large fatty acids and aldehydes. This non-specificity may qualify hOBPIIa as an excellent option to detect concentrations of a wide variety of volatile odorants, since the proteins act as carrier molecules, forming non-covalent bonds with volatile odorant molecules to transport them to the olfactory neurons (Pelosi 2001). There is evidence that they bind volatile, non-pheromone compounds with dissociation constants in the micromolar range (Pelosi et al. 2014). They are of low molecular weight in humans at approximately 18-20 kDa, and are soluble, stable to temperature, pH and proteolytic digestion (Whitson and Whitson 2014). hOBPIIA may be viable as an odorant biosensor because it can be expressed in bacterial systems at low cost and easily purified (Silva et al. 2012). Similar synthetic polypeptides that mimic odor receptors or odorant binding proteins have also been developed for the electronic nose technology (Wu and Lo 2000; Panigrahi et al. 2012).

1.8.3 Fluorophore (1-AMA) Binding with OBPs

1-aminoanthracine (1-AMA) is a fluorophore that modifies the structure and dynamics of certain proteins, including those of the lipocalin family, such as odorant binding proteins. Thus, 1-AMA is commonly used to study the interactions between such proteins and their ligands (Hajjar et al. 2006; Larisika et al. 2015; Löbel et al. 2002; Meillour et al. 2009; Nespoulous et al. 2004; Ramoni et al. 2002; Campanacci et al. 2001; Vincent et al. 2004; Wei et al. 2008). By monitoring fluorescence excitation spectra, Kmiecik and Albani (2010) studied the binding effect of 1-AMA on porcine odorant binding protein structure. Porcine OBP may be homologous to hOBPIIa in some aspects such as binding site and behavior since the two proteins are similar in structure and

function. Kmiecik and Albani (2010) observed fluorescence excitation spectra and the time 1-AMA spends in the excited state before returning to the ground state with the emission of a photon (fluorescence lifetime). Porcine OBP contains one Trp residue at position 16, which contributes to fluorescence (Nespoulous et al. 2004). Results showed that increasing titrations of 1-AMA in 2.7 μM causes a decrease in fluorescence intensity at 340 nm due to the Trp residue and then an increase at 490 nm due to 1-AMA. Since the binding peak of the Trp residue is not altered by the addition of 1-AMA, it is unlikely that it is the binding site for the fluorophore on the protein, confirming another study that suggests the residue is not a part of the binding site (Burova et al. 1999), in which the 1-AMA-OBP complex has a dissociation constant of 5±0.25 μM. The tertiary structure of dimeric porcine OBP is modified by binding 1-AMA at low probe concentrations and fluorophore/protein concentrations ratios.

1.8.4 Biosensor Applications with OBP

Lu et al. (2014) used a layer of honeybee OBP immobilized on the surface of interdigital golden electrodes to detect floral odors and pheromones by electrochemical impedance spectroscopy. They were able to establish a correlation between electrical impedance spectra and the change in the protein conformation when bound versus unbound to a ligand. They used the relative decrease of charge transfer resistance to determine ligand concentration from 10^{-6} to 10^{-3} M. They were also able to model the tertiary structure of the honeybee OBP to investigate the molecular docking that takes place when the ligand binds to the protein (Figure 14). Honeybee OPB contains 6 alpha helices that compose a large and highly hydrophobic binding cavity that can accommodate a variety of ligands.

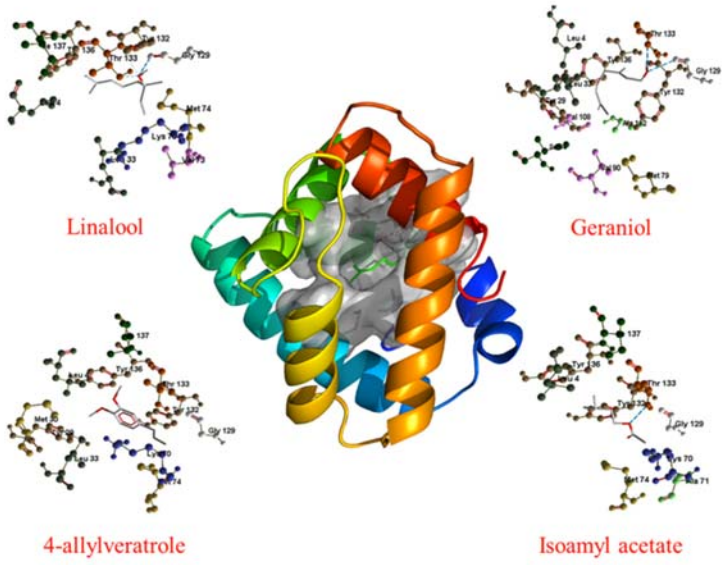

Figure 14. The structure of Acer-ASP2 (in the middle) and the binding modes of four representative ligands to the protein, linalool, geraniol, 4-allylveratrole, and isoamyl acetate (in the periphery) (Lu et al. 2014).

Lu et al. (2014) also found that different ligands lead to different impedance changes (Figure 15), and butanedione was barely detectable because it led to almost no impedance change. They were unable to make their biosensor sensitive enough to detect field gas concentrations of odors since

their biosensor was only able to detect in the mg/m^3 range, and field concentrations were in ng/m^3 range.

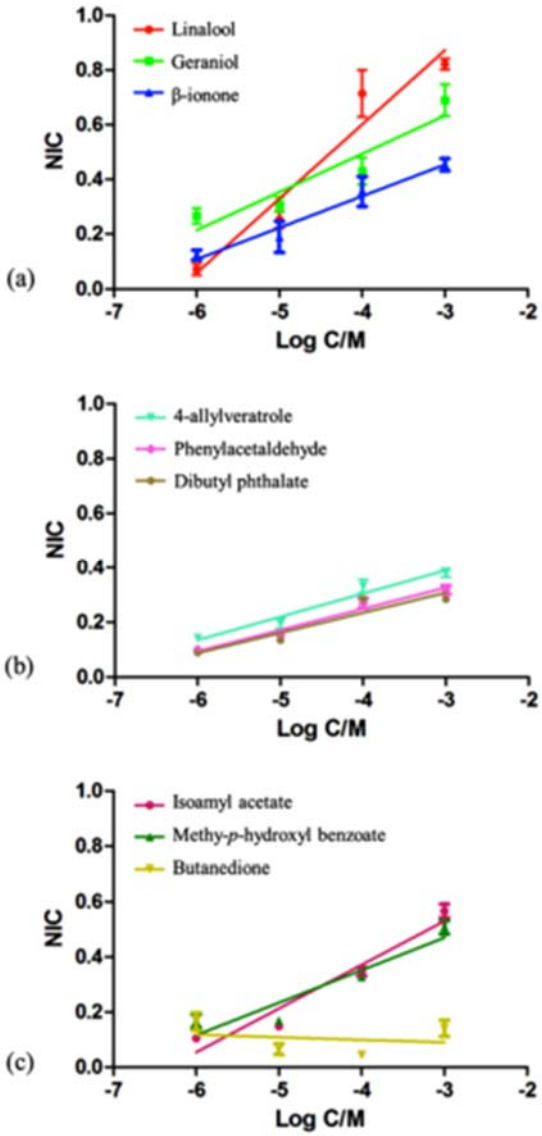

Figure 15. Impedance changes of Acer-ASP2 to different ligands: (a) linalool, geraniol, and β-ionone; (b) 4-allylveratrole, phenylacetaldehyde, and dibutyl phthalate; (c) isoamyl acetate, methy-*p*-hydroxyl benzoate, and butanedione (*n* = 4) (Lu et al. 2014).

Di Pietrantonio et al. (2015) coated surface acoustic wave (SAW) resonators with three different types of OBPs: 1) wild-type OBP from cow, 2) double mutant OBP from cow, and 3) wild-type OBP from pig. The SAW biosensor array system was used to measure concentrations of food flavor vapors, octenol and carvone, in nitrogen atmosphere. The wild type cow OBP was the most sensitive to carvone detection at 9 ppm, whereas the double mutant cow OBP was the most sensitive for octenol detection at 13 ppm indicating that different OBPs are more appropriate

depending upon odorant type and that by combining OBPs, detection assays can distinguish between odorant types. However, none of these tests used hOBPIIa.

1.8.6 OBP for Odor Control

Silva et al. (2014) used pig OBP (pOBP) to control cigarette smoke odor by producing delayed release of fragrances (citronellol, benzyl benzoate, citronellyl valerate and ethyl valerate), from the surface of bleached cotton substrates that were cationized so that the negatively charged pOBP would bind. The researchers wanted to measure the capacity of OBP to retain the fragrances and mask cigarette smoke odor. The affinity of the fluorescent ligand 1-AMA to the recombinant pOBP was measured using a microplate spectrofluorometer with thermoregulation to find the concentration of odorant molecule that would cause the fluorescence to decay to half-maximal intensity. These concentrations (IC_{50} values) are summarized in Table 14.

Table 14. IC_{50} values for studied fragrances determined by competitive binding with 1-AMA-pOBP (Silva et al. 2014).

Fragrance	IC_{50} (µM)	
	25°C	37°C
Citronellol	2.2 ±0.1	3.4 ±0.1
Citronellyl valerate	0.52 ±0.01	0.24 ±0.01
Ethyl valerate	38 ±3	47 ±2
Benzylbenzoate	2.6 ±0.1	–

The relative success of using odorant binding proteins in new and exciting ways has led to the question of whether hOBPIIa could be used as a biosensor to effectively quantify odorants in real air samples using spectrofluorometry.

1.9 OBJECTIVES

One of the aims of this work is to investigate the influence of meteorological conditions on odor complaints from neighborhoods in close proximity to a landfill site, in order to determine the existence of patterns or trends, if any, that could lead to the development of effective odor mitigation strategies. To accomplish this goal, the impact of meteorological conditions of interest (temperature, humidity, wind direction, wind speed, pressure, precipitation, inversions, weather stability class) on the number of odor complaints from two urban solid waste facilities in South Florida were evaluated.

Another objective is to determine whether hOBPIIa complexed in aqueous solution with 1-aminoanthracine displays spectral emission intensity in the presence of H_2S gas that can be correlated to the concentration when measured by spectrofluometry. If it is capable, another objective of this part of the research is to develop a predictive model such that H_2S gas concentration can be determined from the emission intensity reading of a sample of unknown concentration to a degree of certainty that is sensitive enough to be representative of human detection thresholds. Since hOBPIIa has a broad binding affinity, it may ultimately lay the groundwork for using hBOPIIa or a similar analog as a biosensor for municipal solid waste facilities that can measure nuisance odors.

2. METHODOLOGY

The project is divided into two components: 1) understanding the influence of meteorological conditions on odor complaints from neighborhoods in close proximity to a landfill site, and 2) development of a biosensor for detecting hydrogen sulfide using fluorescently tagged hOBPIIa. The following sections detail the research methodology to address these two objectives.

2.1 DATA COLLECTION

The strategy of the first part of this study was to target partner landfills located in an urban setting in Florida. Therefore, several solid waste management entities were contacted in order to collect data about citizen odor complaints. Two different landfill sites located in close proximity to residential communities were selected. Due to the confidentiality of the information provided on odor complaints, any identifying customer information was excluded, and also the identity of the two solid waste facilities participating in the study will remain anonymous. From this point forward, the two sites will be referred to as: 1) Urban Site 1 and 2) Urban Site 2.

Since Urban Site 1 had an existing weather station, real-time access to their weather station was available to provide information on local meteorological conditions. For both sites, historical data on meteorological conditions was collected from the Weather Underground web site (Weather Underground: Weather Forecasts and Reports 2017) for the weather stations that were located physically closest to the landfill's address. Since the wireless real-time weather station at Urban Site 1 was installed in 2008, it could not provide local microclimate information prior to 2008. Therefore, for the previous years, the next closest weather station at the Weather Underground web site was selected to obtain the necessary data. Meteorological data was collected for the following weather parameters: temperature, humidity, pressure, precipitation accumulation, wind direction, wind speed, conditions and events occurred. The odor complaint database for Urban Site 1 was composed of 423 points during the time frame from 2005 to 2016, while Urban Site 2 had a total of 256 points from the same time period from 2005 to 2016. The part of the meteorological data collected is presented in

Table 15.

Table 15. Screenshot of a Selected Part of the Data Used for Meteorological Conditions (Urban Site 1)

Date	No of complaints	Avg T (°F)	Avg H (%)	Avg P (In)	Avg Ws (mph)	Prec Accum (In)	Events
7/5/2005	2	84	72	30.1	7	0	
7/29/2005	1	83	71	30.07	5	0.09	Rain , Thunder storm
8/4/2005	1	84	73	30.01	5	0.19	Rain , Thunder storm
8/5/2005	1	82	81	30.06	4	0.55	Rain , Thunder storm
8/11/2005	2	86	74	30.04	7	T	
8/17/2005	2	87	69	30	7	0	
8/18/2005	1	86	67	30.01	6	0	
8/31/2005	1	85	77	29.93	4	0.23	Rain , Thunder storm
9/13/2005	1	83	66	29.98	7	0	
9/15/2005	1	82	77	30.03	5	0	
9/16/2005	2	84	75	30.05	7	0	
9/24/2005	1	83	72	30.03	11	0	
9/27/2005	1	81	77	29.95	6	0.04	Rain , Thunder storm
10/7/2005	2	81	90	29.69	9	0.4	Rain
10/10/2005	3	81	84	29.79	6	0	

Urban Site 1 and Urban Site 2 each documented odor complaints differently (Table 16 and Table 17). However, there were some similarities in the data collected between the two sites, for instance: date/time of the call, physical location, and the name of the person who made the complaint. Information for the description of complaint, weather conditions at the time of the complaint (only for the wind direction) and findings that landfill personnel have noticed about the odors were inconsistent. If there was too much missing information, that part of the data set was excluded from the further analysis. Also, the missing values were deleted. By looking at the most consistent data that can be used from the odor complaint data sets received, both from Urban Site 1 and Urban Site 2, the following parameters were used: date, time of the call and location of the received complaint. Parameters of interest considered and used for the purpose of the research were:

- Date of the complaint
- Time of the call
- Location of the complaint
- Temperature, °F
- Humidity, %
- Pressure, inches
- Wind direction
- Wind speed, miles per hour
- Precipitation accumulation, inches
- Weather conditions and events present

For reasons of privacy protection and as per the request of the participating facilities, the locations of the complaints were blacked out in both tables.

Table 16. Screenshot of a Selected Part of the Data Received for Odor Complaints (Urban Site 1)

COMPLAI	DATE_CALL_	COMPLAIN_1 LOCATION	ZIP	DEVELOPM	TIME_COMPL	TIME_AM_PM	WIND_DIR_1	WIND_SPEED	DESCRIPTION
Odor	2/19/2013	[redacted]			09:00	AM	SSE	Light	Odor
Odor	7/23/2013								Odors
Odor	10/21/2013							0	Odor
Odor	4/15/2014				09:25	AM	S - SE - SW	Light	[redacted]
Odor	8/1/2014				09:08			Very slight, no real directio	
Odor	9/29/2014				09:50	AM	S	4	Overpowering odor
Odor	1/5/2015				02:30	PM	NNE	18.4	notiiceable odor si
Odor	3/18/2015				10:15	PM	S	2	Odor coming from tl
Odor	12/9/2012				11:30	AM	ESE	5	Odor in yard
Odor	3/29/2014				08:30	AM	SSE	Light	Odors
Odor	3/29/2014				08:45		SSE	Light	Odors
Odor	6/12/2014								[redacted]
Odor	5/24/2014				10:00	PM			odor of methane ga
Odor	9/22/2012				09:00		SSE	Slight	Odors
Odor	9/16/2014				06:00	PM	West SW	Calm	Strong Odor. Never
Odor	7/16/2012				11:30		SSE	0 - 5	Odors more often
Odor	12/15/2013				12:03	AM	SSE	Slight	Odors
Odor	7/17/2012				09:30	PM			
Odor	8/1/2012						SSE	Light	
Odor	9/7/2012				11:30	PM	SSE	Light	Odors
Odor	9/17/2012				11:43	PM	SSE		Odors
Odor	10/2/2013				10:00	PM	S - SE - E - NE	Light	Odor bad
Odor	11/18/2013				10:30	PM	All over	0	Odors
Odor	9/16/2014				09:30	PM	SW - SSW	3 - 4	Odors smelled like
Odor	3/30/2012				06:00	PM			Odors
Odor	3/31/2012				11:59	AM			Odors

Table 17. Screenshot of a Selected Part of the Data Received for Odor Complaints (Urban Site 2)

VIOLATIONCODE	COMPLAINANTLASTNAME	COMPLAINANTFIRSTNAM	COMPLAINANTADDRESS	COMPLAINANTZIPCODE	RECEIVEDDATE	DESCRIPTION
Odor	[redacted]				1/14/2005 11:12:36 AM	Landfill odors.
Odor					1/14/2005	Landfill odors.
Odor					3/7/2005	Landfill odors.
Odor					6/6/2012	Nuisance odors.
Odor					6/6/2012 9:55:13 AM	Nuisance odors.
Odor					4/29/2005 9:05:46 AM	Landfill odors.
Odor					6/14/2012	Nuisance odors.
Odor					4/29/2005	Landfill odors.
Odor					8/28/2012 1:59:01 PM	Nuisance odors.
Odor					11/27/2012	Nuisance odors.
Odor					12/6/2012 12:23:17 PM	Nuisance odors.
Odor					12/14/2012 12:18:06 PM	Nuisance odors.
Odor					12/17/2012 9:45:59 AM	Nuisance odors.
Odor					1/24/2013	Nuisance odors.
Odor					1/24/2013 4:01:30 PM	Nuisance odors.
Odor					2/12/2013	Nuisance odors.
Odor					2/13/2013	Nuisance odors.
Odor					2/12/2013	Nuisance odors.
Odor					4/24/2013 11:13:53 AM	Unconfined emissions.
Odor					5/29/2013	Nuisance odors.
Odor					7/9/2013	Nuisance odors.
Odor					7/18/2013	Nuisance odors.
Odor					7/18/2013	Nuisance odors.
Odor					6/8/2005 3:00:28 PM	Nuisance odors.
Odor					7/23/2013	Nuisance odors.

2.1.1 Urban Site 1

Urban Site 1 is located in an area with flat terrain with highest elevation of 36 feet and a tropical climate with dry winters. Variations in temperature are typically from 59°F to 89°F throughout the year, while temperatures below 46°F and above 92°F rarely occur. Warmer periods (> 89°F) last from June to September, while the cooler period (< 77°F) occurs from December to March, as observed in Figure 16. The period with the clearest days occurs from October to May, while more overcast conditions are prevalent during the summer months. From May until October is the wet season, as well as the windiest part of the year, with average wind speeds of more than 5 mph, and the predominant wind directions are south and east.

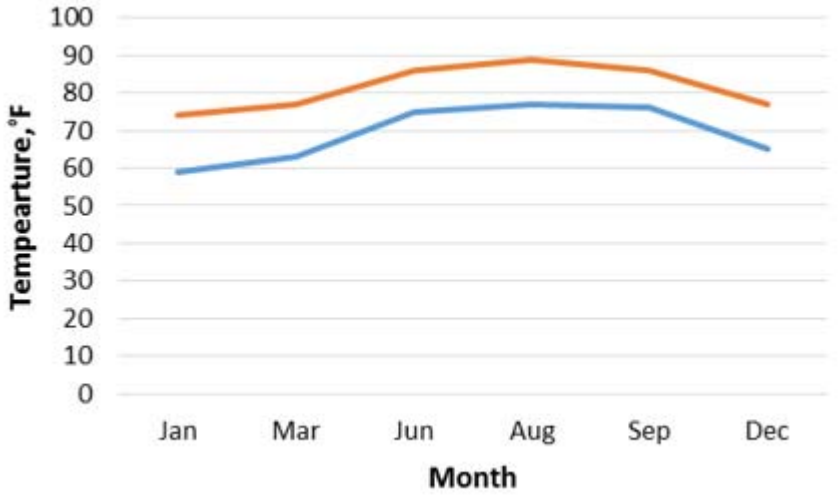

Figure 16. The Daily Average High and Low Temperature for each Month from 01/01/1980-12/31/16: Urban Site 1 (Data obtained from Weather Underground)

Urban Site 1 had an existing weather station installed in 2008 (KFLWESTP21) that records temperature, dew point, wind speed, wind gust, wind direction, precipitation accumulation, and pressure. Real-time access to the weather station was available to provide information on local meteorological conditions (i.e. temperature, humidity, pressure, precipitation accumulation, wind direction, and wind speed). For weather data prior to 2008, the next closest weather station (KFLPALMB134) at the Weather Underground web site (www.wunderground.com) was selected to obtain the necessary data on temperature, humidity, pressure, precipitation accumulation, wind direction, wind speed, and events occurred (thunderstorms, rain, tornado, etc.) (Figure 17).

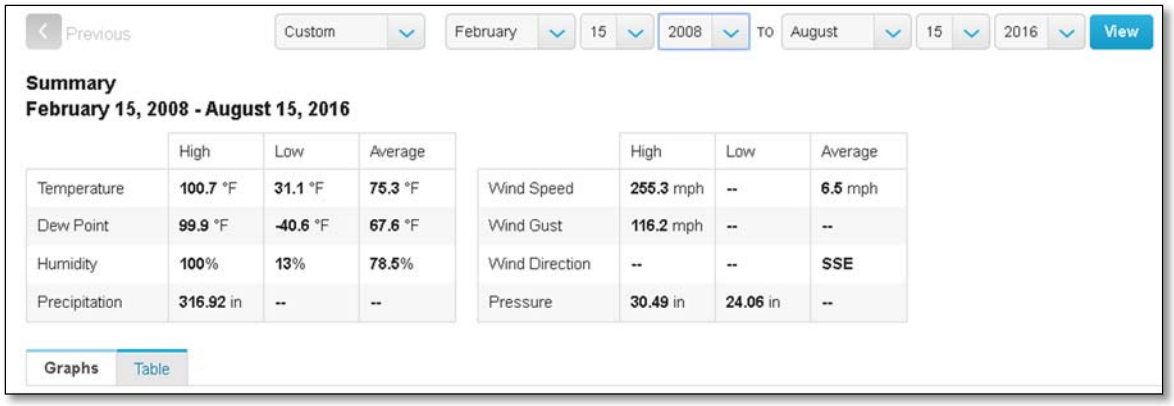

Figure 17. Weather Underground Web Site: Custom Selection of Time Period of Interest (Weather Underground: Weather Forecasts and Report 2017)

The historical growth of the population of Urban Site 1 is 2%/year. Due to the lack of sufficient available free land space, residential communities are being built in close proximity to the existing landfill site. The location of the nearest residential communities surrounding Urban Site 1, as well as the distances are illustrated in Figure 18.

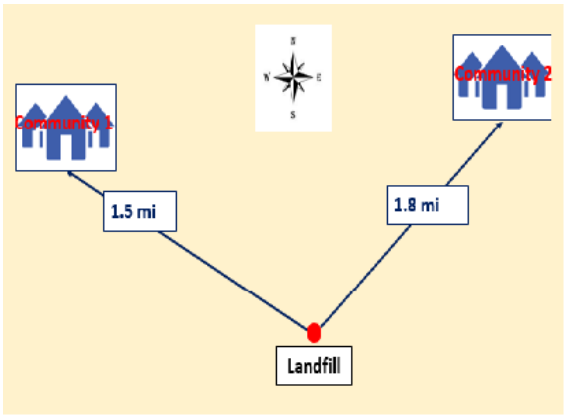

Figure 18. Approximate Locations of Nearby Communities Surrounding Urban Site 1

2.1.2 Urban Site 2

The location of Urban Site 2 is also situated in an area with flat terrain and a tropical climate with dry winters. For this site, the highest changes in elevation are 13 feet, and the warm period (> 86°F) is from June until October, while the cool period (< 78°F) is from December until March (Figure 19). The wet and dry season are in the same time frame as Urban Site 1 (from May to October, and from November to May, respectively). The cloudier period of the year is also during summer months, with average daily wind speed of 5.3 mph. The predominant wind direction in this area, on average, is east.

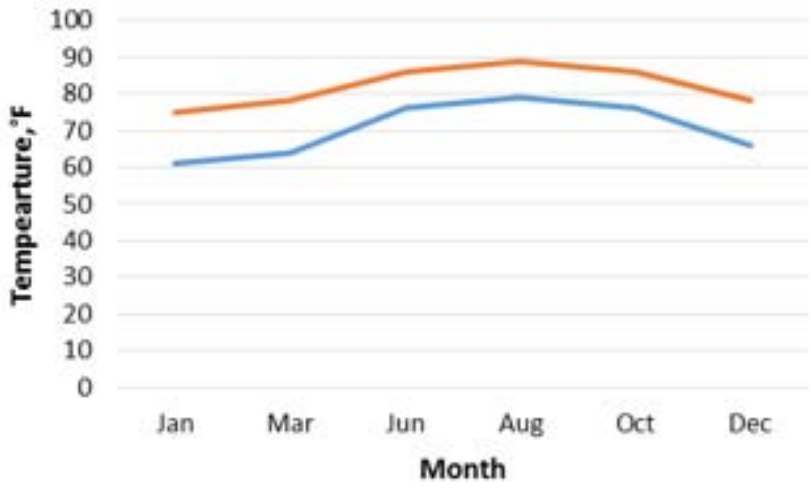

Figure 19. The Daily Average High and Low Temperature for each Month from 01/01/1980- 12/31/2016: Urban Site 2 (Data obtained from Weather Underground)

Installation of a Maximet GMX600 compact wireless weather station from Gill Instruments Limited (Figure 20) provided by FAU iSENSE was arranged with personnel from Urban Site 2 on October 21, 2016, and data collection began on November 2, 2016. Real-time access to the weather station was available to provide information on local meteorological conditions. The wireless weather station provides information on wind direction, wind speed, temperature, humidity, pressure, precipitation intensity, etc. accessible from the intelligent river web portal. After selecting the location, the time period can be selected, and data of interest can be downloaded. For weather data prior to 2008, the next closest weather station (KFLDEERF13) at the Weather Underground web site (www.wunderground.com) was selected to obtain the necessary data.

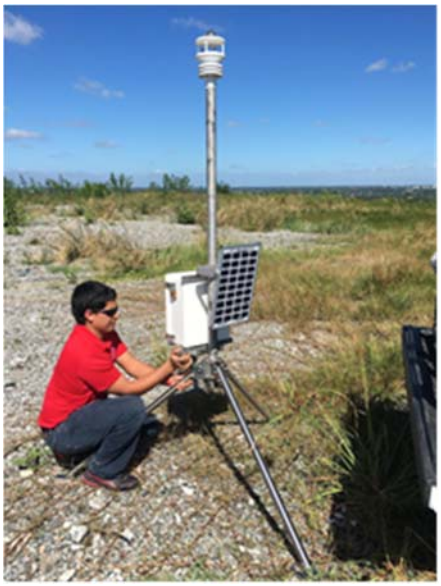

Figure 20. Installation of FAU Wireless Weather Station at Urban Site 2

The historical growth of the population Urban Site 2 is 1%/year. Due to the lack of sufficient available free land space, residential communities are being built in close proximity to the existing landfill site. The location of the nearest residential communities surrounding Urban Site 2, as well as the distances are illustrated in Figure 21.

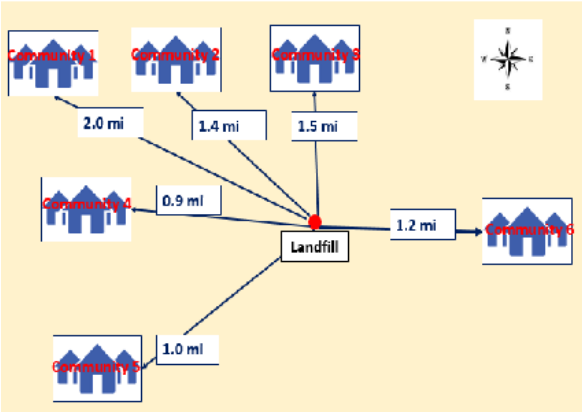

Figure 21. Approximate Locations of Nearby Communities Surrounding Urban Site 2

2.2 PATTERN IDENTIFICATION AND TREND ANALYSIS

Based on the odor complaints data received from Urban Site 1 and Urban Site 2, as well as using appropriate qualifiers for meteorological measurements and landfill operations, the datasets were analyzed to determine the existence of patterns or trends that could lead to the development of effective management strategies. Since real-time access to meteorological data at Urban Site 2 was obtained after the time frame of collected odor complaints data (last date was January 2016), for both sites, historical data (2005-2016) on meteorological conditions was collected from the Weather Underground web site for the weather stations that were located physically closest to the landfill's address (code names: KFLWESTP21, KFLPALMB134, and KFLDEERF13). Data for rainfall/precipitation accumulation was collected for the 24 hours, 3 days, and 7 days prior to an odor annoyance. All other meteorological parameters were collected for the day before the odor complaint. For autocorrelation and PCA (Principal Component Analysis), 1, 2, and 3 days before the odor complaint were considered.

2.2.1 Preliminary Analysis

Microsoft Excel 2013 was used to perform the trend analysis using information about the local meteorological conditions obtained from the weather station located onsite (temperature, humidity, pressure, wind direction, wind speed, precipitation accumulation). The metrological data spreadsheet for Urban Site 1 was shown previously in Table 15. The first step was to filter the data to remove entries with missing values of the parameters of interest (n = 76, or 18% of the data set was incomplete). An analysis was conducted to determine what year, month, day of the week, and time of day had the most odor complaints logged. To that end, the data was first sorted by year and then counted to make that determination. Next, the month with highest number of odor complaints was determined, and the distribution of the received complaints was identified based on the day of the week. The data was then further sorted by month and by day and then counted. The time in the day when the complaint calls tended to occur most often was also determined similarly by grouping data by AM and PM. The next step was to see how many days in the time period from 2005 to 2016 experienced more than one odor complaint in the

same day. Since the partial year 2016 had only three data points, it was excluded from further analysis. From the information gathered in meetings with solid waste facility personnel, three or more verified odor complaints in the same day triggered corrective action(s). For further analysis, dates with 3 or more complaints filed on the same day, presented in Table 18, were investigated.

Table 18. Dates Considered for the Preliminary Analysis for Urban Site 1.

Date	Number of Complaints In the Same Day
12/06/05	6
09/16/14	4
09/18/14	4
09/19/14	6
03/26/15	6

For each of the dates, the physical locations of the odor complaints were plotted to visually verify if the complaints were spread out or if there was a cluster of complaints. Next, the meteorological conditions were examined during the time of the call, as well as for the whole day or the previous day, and additional information was gathered from the nearest weather station or the station installed at the site. Since the weather station at the site did not provide information on meteorological conditions prior to 2008, for the date 12/09/2005, meteorological data was collected from the Weather Underground website, as described earlier, from the next closest location to Urban Site 1.

The second part of the preliminary analysis was conducted when a second odor complaint database was received for Urban Site 2. This data set consisted of 256 files from 2005 to 2016. Each entry provided information on the date and time of the odor complaint, location where the complaint was made, and description of the odor. The inconsistency of the information provided and the incompleteness of the entries contributed to a number of missing values (n = 21 or 8%).

Data from both sites were entered into Microsoft Excel spreadsheets and filtered using the following parameters: date, time and location of the odor complaint. Dates with three or more complaints on the same day were identified for Urban Site 2 in the same way they were for Urban Site 1. To investigate the relationship between the meteorological parameters on selected days, the following parameters were included: air temperature, humidity, pressure, wind direction, and wind speed. Data for each of the meteorological parameters was graphically represented for the day when complaints occurred and compared to the corresponding values for the previous day. Also, values were graphically represented for the exact time when the odor complaint was received and compared to the same time period for the previous day.

The Pearson correlation coefficient (r), which is a measure that explains how well the two datasets are related and if there is a linear relationship between them, is calculated to identify which meteorological parameters may have predictive value based on the previous data. Possible values for Pearson correlation coefficients are between -1 and 1. A high correlation is found if $1>r>0.5$ or $-1<r<-0.5$. Medium correlations are values from 0.3 to 0.5 and -0.3 to -0.5, and low correlation is for r values between 0.1 to 0.3 and -0.1 to -0.3 (Hauke and Kossowski 2011).

Also, relationships between temperature and humidity, temperature and pressure, and humidity and pressure were tested. High correlations (r value near ± 1) would suggest, for example, once today's temperature is known, it can be successfully used to forecast tomorrow's value. If the r value is near 0, there is no discernible relationship. A number one next to the name of the parameter represents the values for the previous day, while a number two next to the name of the parameter represents the values for the day when odor complaints actually occurred.

To assess the applicability of different statistical tools, such as correlation coefficient (R), as well as the Mean Absolute Percentage Error (MAPE), Normalized Root Mean Squared Error (NRMSE) and Mean Squared Error (MSE), it is necessary that the data sets have a normal distribution. This assumption is checked by the Kolmogorov-Smirnov test. Each error statistic has its own advantages and disadvantages; therefore, it has been recommended that simultaneous comparison of some statistics be used to determine the optimal structure (Zhang, Patuwo, and Hu 1998).

2.2.2 Analysis of Isolated Odor Complaints

Based on the collected meteorological data on the days in which three or more complaints were filed on the same day, for both sites (Urban Site 1 = 25 days; Urban Site 2 = 17 days), correlations were calculated for temperature, humidity, pressure and wind speed to identify if there is a correlation in values for every day selected. For example, the values of temperature for every day were compared, and a correlation between them was calculated. The same procedure was done for the rest of the meteorological parameters mentioned. The next step was to compare the actual number of odor complaints received per day with the average value of temperature, humidity, pressure, wind speed and rainfall. Furthermore, the number of complaints was compared to the average value of the same parameters, but in this case the actual time that the complaint was made was taken into consideration. Odor complaints were also separated based on the dry season (November until April) and wet season (May until October) to test the existence of patterns, if any, related to different seasonal variations.

Rainfall data for days with three or more complaints was also analyzed for the 24-hour period prior, three days prior and seven days prior. The next step was to identify any monthly variations. For each of the months where variations were found, historical data for the previous ten years, for that particular month, was obtained and tested for normal distribution by creating a normal probability plot (Q-Q plot). The aim was to single out if that year, by the amount of rainfall received in the month of interest, was an outlier. An outlier is an observation that distinguishes itself from other values in a data set tested. One useful graphical representation in detecting an outlier is creating a box plot. It uses the median and the lower (1st quartile) and upper (3rd quartile) quartiles (ITL 2017). Defining the interquartile, as well as "fences," is required to detect extreme values (outliers). A value that exceeds an inner fence line is considered a "mild outlier," while an observation that exceeds an outer fence is considered an "extreme outlier" (ITL 2017):

- **Interquartile (IQ) = Q3-Q1**
- **Lower Inner Fence = Q1-1.5×IQ**
- **Upper Inner Fence = Q3+1.5×IQ**
- **Lower Outer Fence = Q1-3×IQ**
- **Upper Outer Fence = Q3+3×IQ**

Where,

IQ = Interquartile
Q1 = Lower (1st) Quartile
Q3 = Upper (3rd) Quartile

Analyses conducted included: meteorological data for each of the days with three or more complaints, average values of meteorological conditions for each of the days compared to the frequency of odor complaints, seasonal variations (dry v. wet season), and rainfall data for the day, three days, and seven days prior to an odor event.

2.2.3 Analysis of Dates with No Odor Complaints

To further investigate the tendency of odor complaints to occur in relation to complex meteorological conditions, additional data was needed to supplement the database. Since the collected data sets so far have focused on only the dates when actual complaints were filed, it was decided to investigate the dates on which no complaints were filed instead. For the entire duration of the data set, every date between those with complaints was assigned with a value of 0, representing the absence of odor complaints for that specific date (Table 19).

Table 19. Summary of Total Data Points Included.

Parameter	Urban Site 1	Urban Site 2
Time frame	07/02/05 – 03/18/16	01/11/05 – 09/14/16
Dates without odor complaints	3912	4258
Dates with odor complaints	423	256
Dry season	1951	2101
Wet season	1961	2157

The purpose of adding the dates with no complaints was to investigate if the days with three or more complaints in the same day are distinguishable when compared to the dates when complaints have not been recorded. Meteorological data was collected on temperature (°F), humidity (%), pressure (inches), wind speed (mph), precipitation accumulation (inches) and events (rain, thunderstorm, storm, etc.). The data set was segregated based on the dry (November until April) and wet season (May to October). Seasons were compared to interpret any differences or reveal any conditions that could trigger frequency of odor complaints. Also, an autocorrelation analysis for complaint frequencies, for the whole data set, was performed to define how well the number of odor complaints from the previous day (lag 1 autocorrelation) would forecast the next day's number of odor complaints. Autocorrelation is a correlation coefficient that instead of correlating two different variables, is actually indicating a correlation between two different values of the same variable at times X_i and $X_i + k$ (X = variable, k = time selected). To detect non-randomness, usually the first autocorrelation (lag 1) is used (Autocorrelation 2017). A correlation closer to ±1 would indicate that if today's number of complaints is known, the number of complaints for the next day could be predicted. If the autocorrelation is near 0, there possibility for prediction is low (Figure 22).

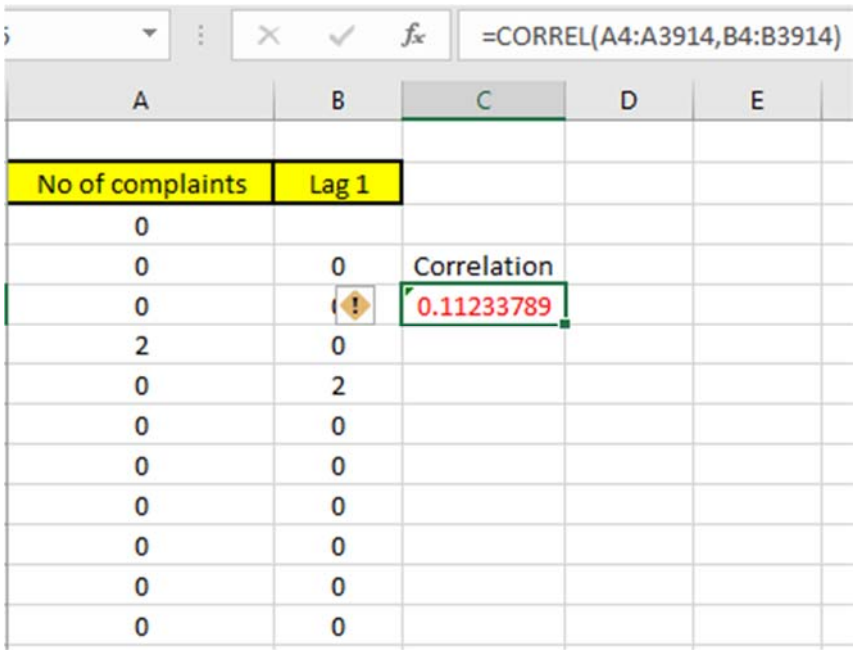

Figure 22. Screenshot of First Autocorrelation Analysis Conducted Using Microsoft Excel (Lag 1)

Analyses conducted included: comparing meteorological conditions on the days with or without odor complaints filed, seasonal variations (dry v. wet season), and autocorrelation analysis.

2.2.4 Analysis of Isolated Days and Random Days with No Complaints but with Similar Weather Patterns

To test the existence of any correlation between meteorological conditions and random days with and without complaints, the same number ($n = 44$) of random days with very similar meteorological conditions to the days with high numbers of complaints were selected. The total number of days with three or more odor complaints in the same day for Urban Site 1 and Urban Site 2 was 27 and 17, respectively. Also, meteorological data was collected for the previous day for both complaint data and selected random days based on similar weather patterns. As an example, the value of temperature for the day the complaint was filed was subtracted from the value of temperature from the previous day. The same procedure was applied to all meteorological parameters (temperature, humidity, pressure, winds speed, and precipitation accumulation) for both random days and days with actual complaints. The dates in which the value was closest to zero were grouped for the analysis.

To identify how often the same weather pattern occurs, both with and without odor complaints, frequencies were calculated based on differences in meteorological values between the day before and the actual day of the complaint or a selected random day when complaints did not occur. Pairs (1 pair = difference in a value when complaint occurred compared to the previous day and difference in a value of a random date compared to the previous day) of the same trend, representing bars going in the same direction, both positive or both negative, were added together and then divided by the total number of pairs. An example calculation for temperature is presented as follows:

$$\Delta T_1 = T_1 - T_1^*$$

$$\Delta T_0 = T_0 - T_0^*, \text{ where:}$$

T_1 = Temperature at the day when complaint was filed

T_1^* = Temperature from the previous day of the day when complaint occurred

T_0 = Temperature for the random day selected with similar weather conditions

T_0^* = Temperature from the previous day of randomly selected day.

ΔT = Difference in values for the day of occurred odor complaint

ΔT_0 = Difference in values for the random day, without odor complaint

T = Total number of points

If both have a positive or negative sign, they create a pair and represent the same weather pattern trend, both whether a complaint was received and not (Table 20). In this case, we can identify 4 pairs going in the same direction, with the total number (T) of pairs being equal to 6. By dividing those two values and multiplying by 100, the result of 66.6% frequency of temperature values being similar on the days when complains have and have not occurred, is achieved.

Table 20. Sample Calculation to Identify Frequency of Same Weather Patterns, Both With and Without Odor Complaints

ΔT	ΔT_0
-1	-5
0	4
6	1
3	4
2	-6
3	-9

Frequency, % = 4 pairs/T = (4/6) × 100 = 66.6%

To investigate how the wind direction is related to odor complaints, data was collected for every day when there was a complaint, as well as for the random days previously selected (Table 21).

Table 21. Summary of Data Points Included in the Analysis of Isolated Days Versus Random Days with Similar Weather Conditions

Parameter	Urban Site 1		Urban Site 2	
	With Complaints	No Complaints	With Complaints	No Complaints
Number of days	27	27	17	17
Wind direction	596	636	402	474
Wind speed	596	636	402	474
Weather conditions	600	642	404	434*
Events	600	642	404	450

*Data included also points marked as "Unknown" (n = 16), so those points were excluded from the analysis.

Also, wind speed was included in the analysis to determine the most frequent wind speeds that occur in each scenario. The most common method for characterizing wind speeds is the Beaufort scale (Beaufort Scale 2017); therefore, the Beaufort wind speed scale is ummarized in Table 22, was used to categorize wind speeds in the data sets.

Table 22. The Beaufort Wind Speed Scale (Beaufort Scale 2017)

Beaufort Number	Description	Wind Speed mph
0	Calm	<1
1	Light air	1-3
2	Light breeze	4-7
3	Gentle breeze	8-12
4	Moderate breeze	13-18
5	Fresh breeze	19-24
6	Strong breeze	25-31

Some data entries had wind speed points described as “Calm”, so those points were replaced with 0.9 mph since, based on the Beaufort scale, “Calm” wind speed is below 1 mph. All hourly values for wind speeds were sorted based on a specific speed and attributed to the appropriate speed range, according to the Beaufort scale. From the obtained data, six wind speed ranges have been classified: <1 mph, 1-3 mph, 4-7 mph, 8-12 mph, 13-18 mph, 19-24 mph, and 25-31 mph.

The frequency of each wind direction was calculated based on the total count of that particular wind direction divided by the total number of all wind direction points in the data set. The values used were hourly values for each of the days selected. Frequencies were computed as follows:

$$Frequency,\ \% = (X_i / Y_T) \times 100\%, \text{ where:}$$

X_i = Count of how many times a specific wind direction was observed at a specific wind speed

Y_T = Total count of points in the dataset

The values were expressed in percentages. The same was done for the wind speed categories. Wind direction and wind speed together would reveal which combination tended to occur the most often. The most frequent wind directions and wind speeds were compared to those on the days where there were no odor complaints. Communities where most of the complaints were received were identified and compared to the predominant wind directions. Weather conditions, as well as the events for the days with complaints and with the absence of same, were also compared. Weather conditions described if, on the day of the complaint or absence of same, the conditions were: clear sky, scattered clouds, mostly cloudy sky, etc. Events described (if present) included: thunderstorms, rain, no rain, etc. Frequency was calculated based on the amount each condition or event occurred and divided by the total number of observed values.

Analyses conducted included: random days with no odor complaints with similar meteorological conditions as the days with three or more complaints in the same day; wind speed and direction

compared for both scenarios, with or without odor complaints; and weather conditions and events on days with or without odor complaints.

2.2.5 Correlation Matrix, Principal Component Analysis (PCA) and Linear Regression

XLStat® was used for more advanced computing such as correlation analysis, principal component analysis (PCA), and linear regression to evaluate the relationship between parameters. The first task was to use all the data to create an understanding of the number of data points and to eliminate missing data.

Correlation analysis indicates whether the variable is related to other variables on an individual basis. The benefit of this analysis is to identify parameters that are clearly correlated. However, this works best when there are a limited number of variables. For this analysis, there were 18 variables:

- Number of complaints: number of files reported in any given day (most commonly 0)
- Days -1: lag of 1-day from the previous with regard to complaints
- Days -2: lag of 2-days from the previous with regard to complaints
- Days -3: lag of 3-days from the previous with regard to complaints
- Temperature High for the given day
- Temperature Chg: change in high temperature from the prior day
- Temperature Avg for the given day
- Temperature Low for the given day
- Humidity High for the given day
- Humidity Chg: change in average humidity from the prior day
- Humidity Avg for the given day
- Humidity Low for the given day
- Pressure High for the given day
- Pressure Avg for the given day
- Pressure Low for the given day
- Wind Speed Avg for the given day
- Wind Speed Low for the given day
- Precipitation for the given day

Note that hourly or more frequent data was not available.

Because there were so many variables, it was likely that each contributes a small amount, and those variables that are actually correlated (and therefore measure the same thing), may not be exposed by this analysis. Hence, a more complex multivariate analysis was suggested. Data was first modified so that there were no zeros within the data set. Any zeros left in the data set will cause some statistical tests to either fail to calculate or output invalid solutions. The next step was cleaning up the data to remove any place that lacked data as the absence of data would also be interpreted as a zero within the data set. After this process, there were 3910 entries remaining with complete data for the analysis.

Given the large number of variables (18), principal component analysis (PCA) was used to reduce the number of variables. PCA does this by creating an orthogonal transformation of the data using eigenvalues and eigenvectors. The orthogonal transformation provides a series of "factors," which are combinations of the larger set of variables used. For example, a factor might combine all temperature, humidity or even all weather data if variation in that data

explains the variations in the parameter of concern. In this case the parameter of concern is odor complaints, so weather and other data can be mined to find out which ones might contribute more to the variance and which ones measure the same things (those would be part of a given factor based on correlations). The goal is to reduce the 18 variables to a very few that explain most of the variance. PCA takes the variables and determines combinations of factors that create the best fit for the observation set. A Scree plot is used to determine how many factors create 70% of the variation. The aim is to find a smaller number of interpretable factors that explain the maximum amount variability in the data set. With PCA, all factors in excess of 1.0 are kept. Those with factor values under 1.0 are assumed to contribute little to the overall explanation of the results and can be neglected. It is desirable that the factors represent at least 70% of the resulting eigenvalues. Once the factors are identified, eigenvalues are analyzed to determine which set of variables contributes most to the factor. Ideally, the investigator should look for values that are greater than 0.6 – 0.7.

A Varimax diagram is used to visualize which factors are correlated and how strongly. It shows vectors pointing away from the origin to represent the original variables. The angle between the vectors is an approximation of the correlation between the variables. A small angle indicates the variables are positively correlated, an angle of 90 degrees indicates the variables are not correlated and an angle close to 180 degrees indicates the variables are strongly negatively correlated (Smith 2002). The length of the line from the center of a Varimax plot indicates the variable's contribution to the overall analysis. If the line is short, the variable has little impact on overall variability (Smith 2002).

A regression model was also performed in order to estimate the relationship among variables. XLStat® can also be used to generate a linear regression equation that can confirm some of the PCA findings. The concept is to create a weighted equation whereby one can predict results based on the factors included in the regression equation. However, unlike PCA, all the variables are included. Hence strongly correlated variables would have less weight individually since they measure the same thing (the idea with PCA is to use the factors to find surrogates). This technique is used for modeling equations and analyzing several variables at once when the focus is on a relationship between a dependent variable and multiple independent variables. In this case, the dependent variable is the number of odor complaints, and the independent variables are related to the meteorological conditions of interest. Based on the dependent variable being numbers of odor complaints, the linear regression and PCA allow for investigation of which independent variables create the variability in the number of complaints each day. The fact that most days are zero does suggest challenges if the days preceding the complaint are similar to the day the complaint was received. This is why variables for t-1, t-2 and t-3 days were created.

2.3 BACTERIAL EXPRESSION OF HUMAN ODORANT BINDING PROTEIN IIA (hOBPIIA)

2.3.1 Method 1 of Bacterial Expression of hOBPIIA

A bacterial expression plasmid absorbed on filter paper was obtained from Artur Ribeiro, Professor of Biological Engineering at the University of Minho in Braga, Portugal (Silva 2013). The plasmid DNA contained the coding sequence for hOBPIIa. The plasmid had been cloned prior to shipment into the pET-28 expression vector with a kanamycin drug selection marker and a Hexa-His affinity tag. The Hexa-His affinity tag indicates that a polyhistidine tag is the

facilitator during affinity purification of the recombinant protein expressed in *E. coli*. Figure 23 indicates restriction endonuclease sites used to clone the gene of interest into this vector.

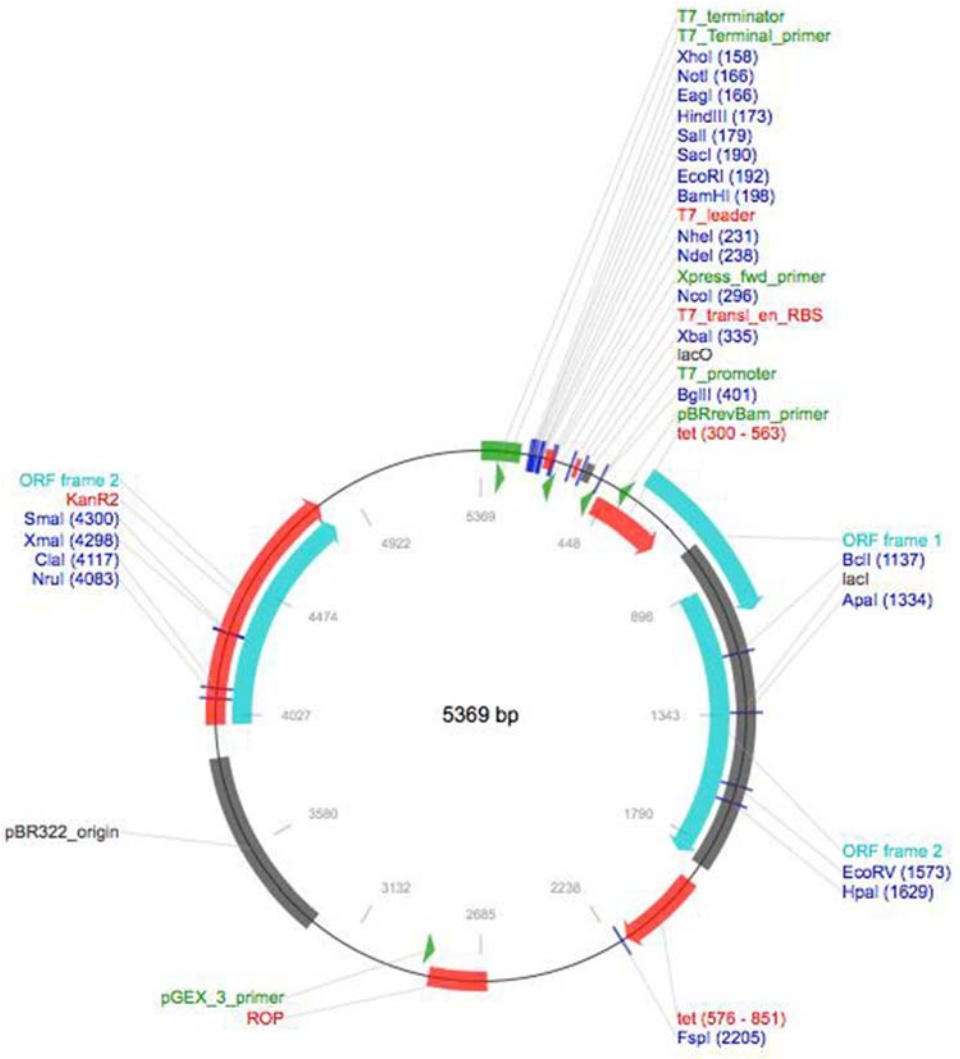

Figure 23. Generated plasmid map for pET28a vector (www.addgene.org/vector-database/2565/)

The nucleotide sequence (513 nt) that encodes the amino acid sequence of hOBPIIa (https://www.ncbi.nlm.nih.gov/CCDS/CcdsBrowse.cgi?REQUEST=CCDS&DATA=CCDS6992) is represented as follows:

ATGAAGACCCTGTTCCTGGGTGTCACGCTCGGCCTGGCCGCTGCCCTGTCCTTCACC
CTGGAGGAGGAGGATATCACAGGGACCTGGTACGTGAAGGCCATGGTGGTCGATAA
GGACTTTCCGGAGGACAGGAGGCCCAGGAAGGTGTCCCCAGTGAAGGTGACAGCCC
TGGGCGGTGGGAACTTGGAAGCCACGTTCACCTTCATGAGGGAGGATCGGTGCATC
CAGAAGAAAATCCTGATGCGGAAGACGGAGGAGCCTGGCAAATTCAGCGCCTATGG
GGGCAGGAAGCTCATATACCTGCAGGAGCTGCCCGGGACGGACGACTACGTCTTTT
ACTGCAAAGACCAGCGCCGTGGGGGCCTGCGCTACATGGGAAAGCTTGTGGGTAGG

AATCCTAATACCAACCTGGAGGCCCTGGAAGAATTTAAGAAATTGGTGCAGCACAA
GGGACTCTCGGAGGAGGACATTTTCATGCCCCTGCAGACGGGAAGCTGCGTTCTCGA
ACACTAG

Translation(170aa):
MKTLFLGVTLGLAAALSFTLEEEDITGTWYVKAMVVDKDFPEDRRPRKVSPVKVTALG
GGNLEATFTFMREDRCIQKKILMRKTEEPGKFSAYGGRKLIYLQELPGTDDYVFYCKDQ
RRGGLRYMGKLVGRNPNTNLEALEEFKKLVQHKGLSEEDIFMPLQTGSCVLEH

Figure 24 indicates restriction of endonuclease sites used to clone the gene of interest into this vector.

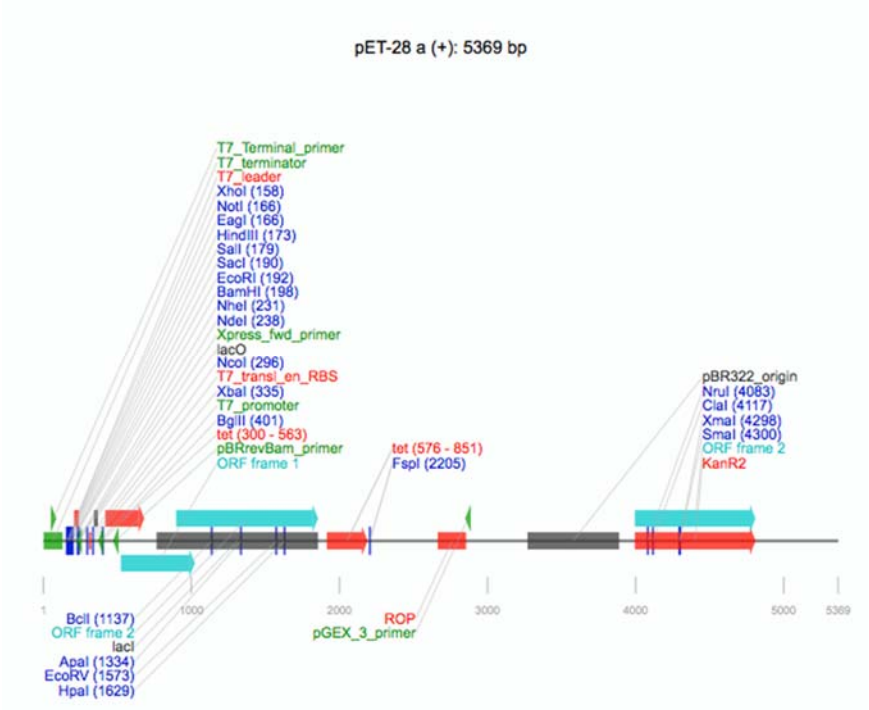

Figure 24. Linear map of analyze sequence: pET-28 a (+)[3]

The plasmid was eluted from the filter paper using Trizma-Ethylenediaminetetraacetic acid (Tris-EDTA/TE) buffer in a heat sealable plastic bag using a Clamco Impulse Sealer (Model 210-12E) to maintain a minimal volume. The buffer solution was allowed to saturate for 24 hours at 4°C. Following incubation, the eluted plasmid-Tris-EDTA buffer solution was stored at -80°C. Finally, the plasmid was isolated and concentrated using ethanol precipitation, centrifugation, and removal of ethanol as follows. The sample that should have contained the plasmid was added to a microcentrifuge tube with Tris-EDTA buffer to a volume of 90 µL. Then 10 µL of 1 mg/mL glycogen (ultrapure molecular biology reagent grade) was added to ensure that even miniscule amounts of nucleic acid would be precipitated. Next, 10 µL of 7.5 M NH_4OAc and then 375 µL of ethanol were added and vortexed to mix thoroughly. The solution was chilled at -80°C for 10 minutes, centrifuged at full speed for 15 minutes, and then the ethanol phase was decanted completely. The pellet was resuspended in 17 µL of nanopure water so that there would be no ions to interfere with electroporation, which would reduce efficiency. The reason nanopure water was used in culturing was because it has a very low bacterial content

compared with deionized water so there is less chance for bacterial contamination of the culture.

A culture of *E. coli* expression strain XL1 Blue II was grown in overnight culture to serve as an expression vector for the DNA plasmid. The DNA was added to the concentrated *E. coli* culture and electroporated using a Bio-Rad MicroPulser™. Transformants were inoculated onto Kanamycin Luria Broth Agar plates and incubated at 37°C. A single colony, isolated from each plate, was used to inoculate separate 10 mL test tubes of Luria Broth (LB) medium and grown at 37ºC with shaking (approximately 250 rpm), until the media reached an optical density (OD) of 0.3 – 0.4 at λ = 600 nm. At this density, the metabolism and cell growth was halted by incubation on ice for 5 minutes. The cell suspension was centrifuged at 3000 rpm (1100 G) for 10 minutes at 4ºC. The supernatant was discarded, and the pellet was resuspended in 1 mL of cold (~4°C) 1X transformation and storage solution containing polyethylene glycol, dimethyl sulfoxide, and divalent cations in bacterial growth medium. About 1 – 10 ng of plasmid in a final volume of 1 – 10 µL was added to the cellular suspension, which was kept on ice for one hour. Then cells were heat shocked at 42ºC for 2 minutes and then stopped by immersion in ice for 2 minutes. Next, 1 mL of warm (~37°C) LB was added, and the suspension was incubated for one hour at 37ºC with shaking (~250 rpm) to activate and express the gene of interest that confers resistance to the Kanamycin selective marker. Lastly, 50 – 200 µL of the transformation mix was plated on LB-agar-kanamycin plates and incubated for 16-20 hours at 37ºC.

2.3.2 Method 2 of Bacterial Expression of hOBPIIa

A transformed BL21 *E. coli* strain was provided by Artur Ribeiro, Ph.D. already containing the plasmid coding for hOBPIIa. Instead of transforming plasmidic DNA into *E. coli* as in Method 1, transformants were pre-prepared and sent as agar stabs, which is a very stable format in which to transport clones. Since there were ~20 agar stabs in separate microcentrifuge tubes, clones from each tube were kept separated throughout the expression process in case of any differences between them. The *E. coli* transformants were incubated overnight on LB-agar-kanamycin plates at 37°C. Following incubation, colonies were inoculated into fresh LB media. An overnight culture was prepared with 50% glycerol and frozen at -80ºC for use indefinitely.

Another overnight culture was grown by inoculating four 5 mL test tubes of LB with the frozen stock. Again, multiple tubes were used and kept separated throughout the expression process in case of any differences between them. Tubes were incubated overnight in a shaking water bath incubator (~250 rpm) (Figure 25).

Figure 25. Overnight culture grown from frozen stock; Four Eppendorf tubes were chosen from the frozen stock and each had their own test tube

Powdered kanamycin sulfate (Thermofisher catalog # 11815024) was added to nanopure water and filter sterilized by adding the solution to a sterile 30 mL single-use syringe (Henke, Sass, Wolfe) with a 25 mm sterile 0.2 µm nylon syringe filter (Fisher). The following day, four 250 mL flasks of 50 mL fresh LB media combined with filter sterilized kanamycin sulfate at a final concentration of 30 µL/mL were inoculated with the overnight culture at a ratio of 1:100 and placed in a shaking water bath incubator at 37ºC and ~250 rpm until early/mid log growth phase was achieved of approximately $OD_{600\ nm} \approx 0.4$.

Since the gene is under the control of the lac operator, isopropyl β-D-1-thiogalactopyranoside (IPTG) was used for induction because it mimics allolactose and triggers transcription. Therefore, following incubation, three of the cultures (labeled 2, 3, 7) were induced with 0.1 mM IPTG and the fourth (labeled 7c) was uninduced as a control (refer to Figure 25). Incubation continued for approximately 6 hours, after which cells were transferred to 50 mL conical centrifuge tubes and harvested at 2,000 rpm for 10 minutes at 4ºC. The supernatant was decanted (Figure 26).

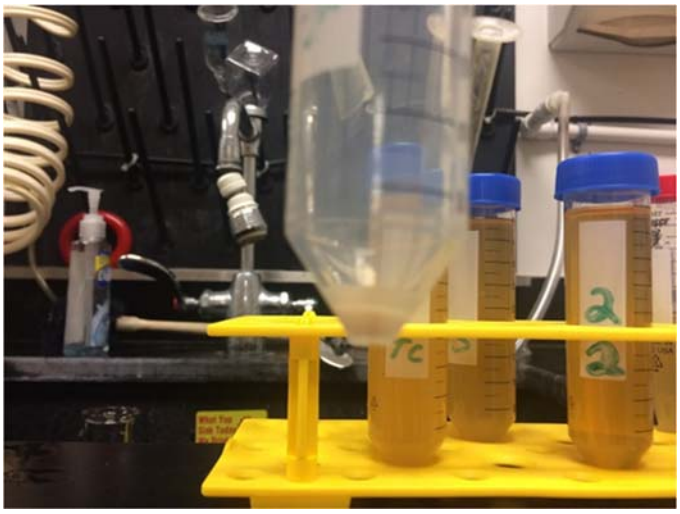

Figure 26. The washed cell pellet is in the tube in the foreground, and the induced and uninduced control tubes in the background were yet to be decanted and washed.

The pellet was washed again in 2 mL Buffer A (50 mM Tris-CL pH 7.5, 150 mM NaCl), decanted again and resuspended in 1 mL of Buffer A. Suspended cells were transferred to microcentrifuge tubes and frozen at -80ºC.

2.3.3 Protein Purification

Frozen cells were brought to room temperature and lysed by sonication on the maximum power setting with a Misonix XL-2000 Series Sonicator for three pulses of 15 seconds each, and placed on ice for cooling between each round (Figure 27).

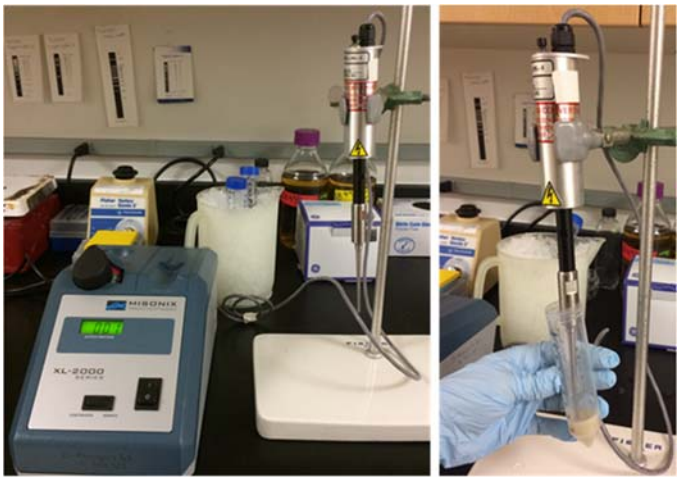

Figure 27. Misonix XL-2000 Series Sonicator was used on the maximum power setting to lyse cells and extract cell contents

In a fourth round, cells were sonicated for 60 seconds. Cellular debris was removed by centrifugation at room temperature for 30 minutes at 8,000 rpm. Next, 1 mL aliquots of supernatant were decanted into sterile microcentrifuge tubes. The cell pellet and supernatant were frozen separately at -20°C to be analyzed with 15% SDS-polyacrylamide gel electrophoresis (SDS-PAGE) to ensure that a protein of approximately 18-20 kD was being

produced in sufficient quantities by the system (as verified by visual inspection) and to ensure that the protein was remaining soluble in the supernatant rather than stuck in the cellular debris.

Prior to analysis with SDS-PAGE, a Bradford Assay (**Figure 28**) was performed with the supernatant to determine the protein concentration of the stock according to the method of Bradford (1976). A set of protein standards containing 2, 4, 6, 8, 10 and 12 µg of 2 mg/mL bovine serum albumin (BSA) stock were added to separate microcentrifuge tubes, diluted to a final volume of 800 µL with deionized water. Then, 200 µL of 5X Bradford reagent was added, mixed by vortexing, and incubated for at least 5 minutes at room temperature. The $OD_{595\ nm}$ of each sample was measured using a Jenway 6305 spectophotometer to generate a Bradford standard curve. Then 2 µL each of the uninduced and induced extracts were added to separate microcentrifuge tubes containing 798 µL deionized water and 200 µL 5X Bradford reagent (Comassie Blue G-250) and incubated for 5 minutes at room temperature. $OD_{595\ nm}$ readings of each sample were compared to the Bradford standard curve to determine the concentration of proteins that contained aromatic amino acids. The Bradford assay specifies the use of 595 nm for the optical density measurement. This is slightly different than the wavelength (600 nm) used to estimate *E. coli* growth density.

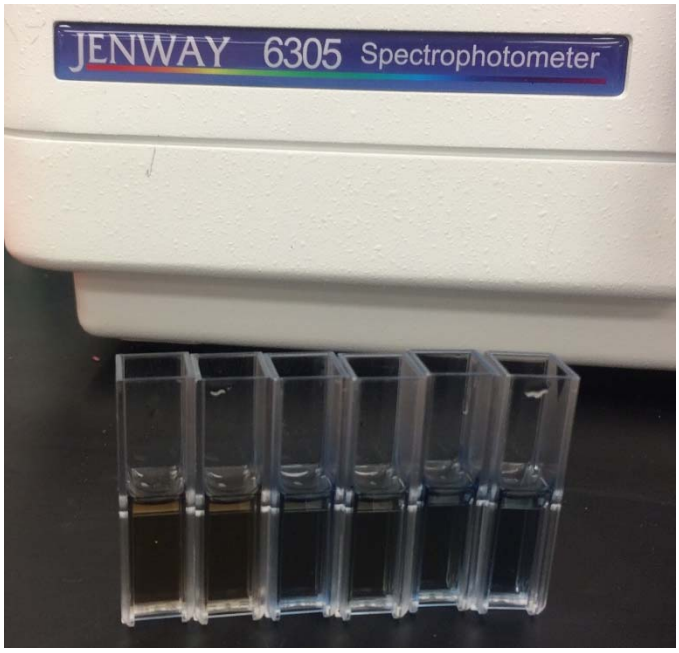

Figure 28. Cuvettes showing color gradient of Bradford standards from 1 to 6 mg of BSA from left to right; the intensity of blue of the solution increases with aromatic amino acid concentration

Following the Bradford Assay, pellets and supernatants of the induced and uninduced extracts were run on a 12.5% polyacrylamide gel in a Bio Rad electrophoresis gel box (Figure 29) with 1X running buffer to observe whether the protein was of the expected size (18-20 kDa) and whether it was soluble in the supernatant or remained trapped in the cell pellet, potentially inaccessible in inclusion bodies.

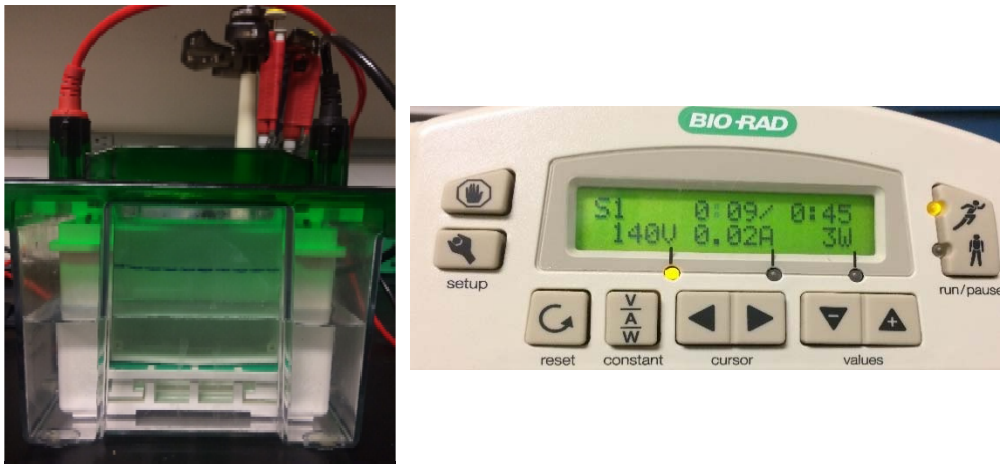

Figure 29. Bio Rad electrophoresis gel box containing SDS-PAGE loaded with samples (left) and settings during the run (right)

For SDS-PAGE electrophoresis, the following reagents were used: 1X running buffer, 4X loading dye, and 10X blotting buffer. SDS-PAGE 12.5% resolving gel and 4% stacking gel were assembled in the gel box. 1X running buffer was added to the inside and outside reservoir. Reagents were prepared as described in Table 23.

Table 23. Recipes for SDS-PAGE stock solutions

1X running buffer		
	60 g	of Tris Base
	288 g	of glycine
	20 g	of SDS
Initially dissolve in	1 liter	
Add to a final volume of	20 liter	of deionized water
4X loading dye (with 2-mercaptoethanol)		
	0.8 g	of SDS (8% final concentration)
	2.5 ml	of 1.0 M Tris•CL, pH 6.8
	4.0 ml	of glycerol
	2.0 mg	of bromophenol blue dye (BPB)
Add deionized water to a final volume of	10 ml	
10X blotting buffer (with 2-mercaptoethanol)		
	58.13 g	of Tris base (480 mM)
	29.30 g	of glycine (390 mM)
	3.75 g	of SDS (0.375%)
Add deionized water to a final volume of	1 liter	
1X TTBS buffer		
	8.0 g	NaCl (136 mM final)
	0.2 g	KCl (2.7 mM final)
	3.0 g	Tris base (25 mM final)
	1 ml	Tween20 (0.1% final)

The volume of sample loaded into the gel wells depends on the results of the Bradford Assay since approximately 20 µg of protein per sample is needed to achieve a strong signal on the gel

and since each well can hold a maximum of 20-24 µL of fluid. For comparison purposes, Novex SeeBlue kaleidoscope standard (4 µL) was loaded into the first well. The samples on ice were brought to room temperature, and 4X loading dye was added to the samples. Next, samples were heated for 2 minutes at 68ºC and then placed on ice. Using a gel-loading tip on a 10 µL pipette, 6 µL of "rainbow" marker was slowly loaded into the first lane. After the samples were loaded, the top of the gel box was attached and run at 180 V for 80 minutes.

If confirmation was obtained that the protein remained soluble and was of the expected base-pair length, protein purification was performed using the cobalt-based immobilized metal affinity chromatography (IMAC) medium (GE Healthcare). His SpinTrap TALON®, which is a single-use column for histidine-tagged proteins and comes prepacked with 100 µL TALON® Superflow™ cobalt-IMAC medium, was used. The advantage of cobalt rather than nickel-charged media is that it is more selective, resulting in higher purity. Approximately 1 mg histidine-tagged protein/column can be purified with the His SpinTrap TALON® columns (Figure 30), and each column produces about 0.5 mL of protein in solution.

Figure 30. His SpinTrap TALON® columns (GE LifeSciences)

Gravity flow is used to perform the four step purification process (Figure 31).

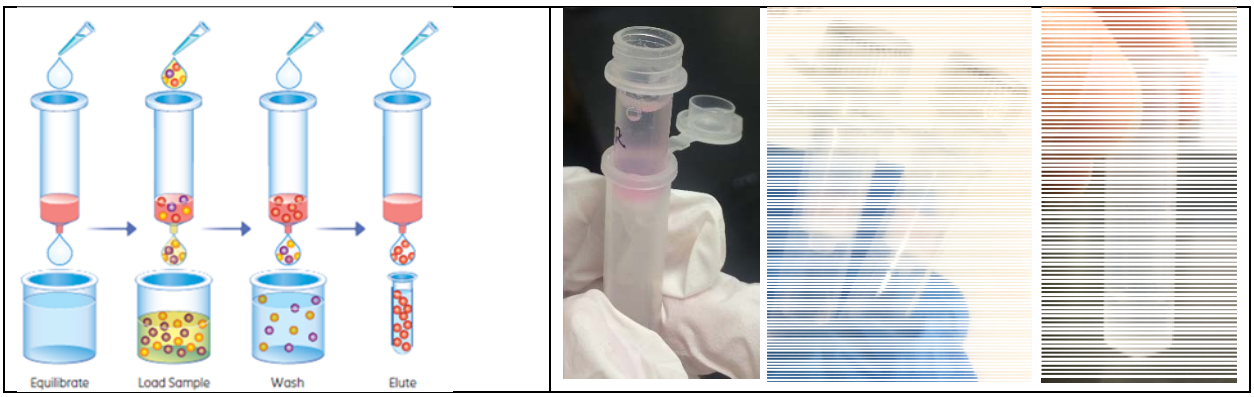

Figure 31. Four-step process for purifying histidine-tagged proteins on His SpinTrap TALON® (schematic on the left, provided by GE LifeSciences), column contents during purification (2nd and 3rd photo), and purified protein directly following the final elution step (right photo)

Following purification, a Bradford Assay and SDS-PAGE electrophoresis was performed on the purified protein and compared to the induced and uninduced cell extract (pre-purification control). Finally, protein production was scaled up to cultures of several liters. Following each

purification, purified protein was analyzed by the same methods of Bradford Assay and SDS-PAGE electrophoresis, as described earlier. It was essential to know the protein concentration of each pure sample to determine the concentrations of proteins used in subsequent tests of the biosensor.

2.3.4 Exposure Chamber

An experimental exposure chamber was constructed using two one-way check valves, 0.25-inch internal diameter flexible polyethylene tubing and a 250 mL HDPE sample bottle (Figure 32).

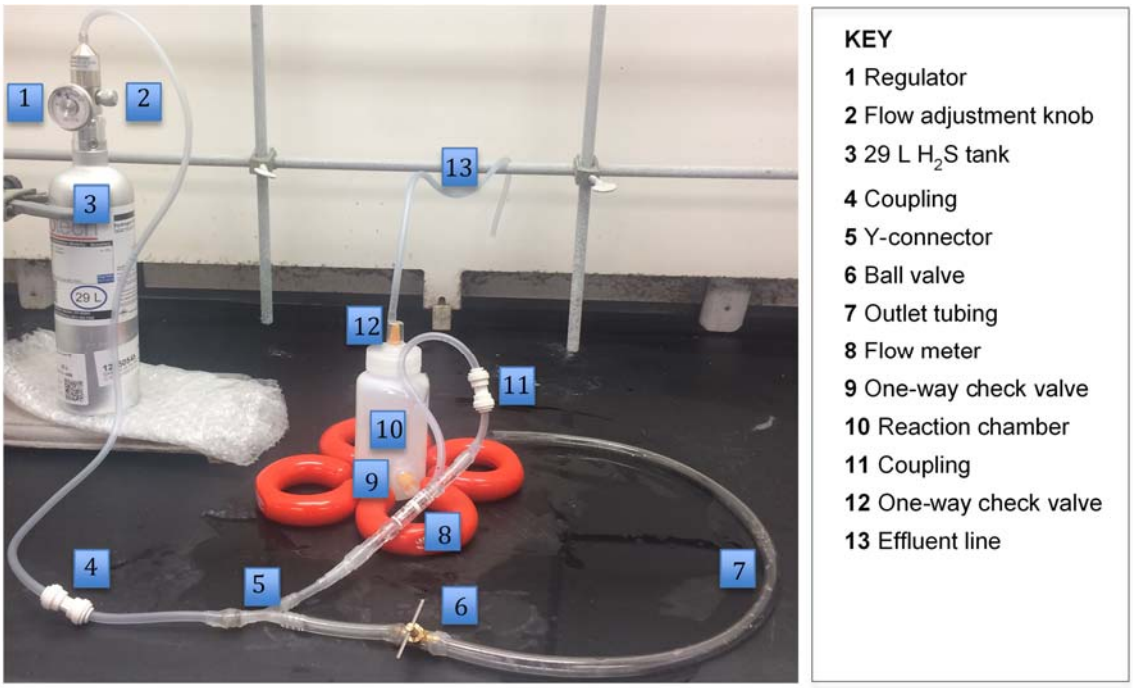

Figure 32. Labeled photograph of the prototype exposure chamber

A measured amount of aqueous hOBPIIa protein-fluorophore complex in buffered solution (100 mL) is placed in the exposure chamber. A Y-connector in front of the flowmeter joins the pressurized gas cylinder with a one-way ball valve for fine adjustment of flowrate. A 29 L gas cylinder delivers hydrogen sulfide gas (25 ppmv ± 5%) balanced with nitrogen (N_2) into the system. Gas escapes through the top of the chamber via a second one-way check valve. After the gas exposure period, an aliquot of liquid sample is transferred by pipette to a 1 cm quartz cuvette for analysis by fluorometry to quantify binding and establish a relationship between concentration and fluorescence.

2.3.5 Competitive Binding Assay

1-aminoanthracene (1-AMA) is an intrinsic fluorophore that was used to observe competitive binding of hOBPIIa to the target odorant, hydrogen sulfide. By monitoring fluorescence excitation spectra, Kmiecik and Albani (2010) studied the binding effect of 1-AMA on odorant binding protein structure. Results showed that the conformation of hOBPIIa is modified by binding 1-AMA at low probe concentrations and fluorescence excitation spectra incurs a red shift.

The first trials were conducted in 50 mM K_3PO_4-KOH, pH 7.5 buffer solution with 1 μM

hOBPIIa and 2 μM 1-AMA. Due to its hydrophobicity, 1-AMA powder (Sigma-Aldrich) was dissolved in a small volume of 100% methanol and then diluted with deionized water to a final methanol concentration of 10%. The stock solution was kept in an amber glass bottle since 1-AMA is light sensitive. Then 100 mL of buffered solution of the protein-fluorophore complex was poured into the reaction chamber and exposed to 25 ppmv hydrogen sulfide gas from the pressurized cylinder at a rate of 0.5 Lpm. Using an aquarium-grade, pumice stone bubbler increased the surface area of solution exposed to the gas. At 30, 50, 60 and 120 seconds of exposure, 1 mL aliquots were removed from the solution by pipette. Each aliquot was transferred separately from its microcentrifuge tube into a quartz cuvette for analysis by spectrofluorometry using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer with FluorEssence software (Figure 33). Samples were excited at 380 nm, and spectral emission readings were recorded between 410 – 700 nm. Slit widths were 5 nm for both excitation and emission.

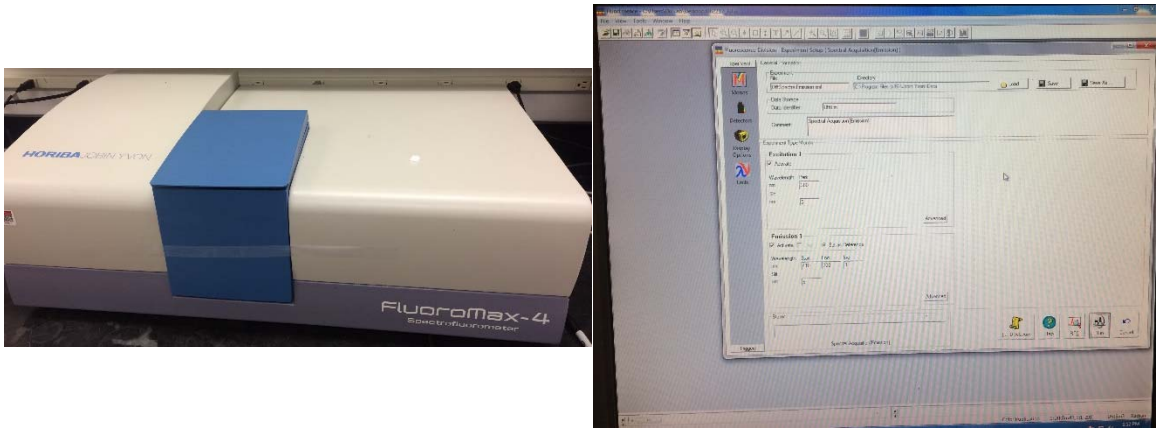

Figure 33. Horiba Jobin Yvon FluoroMax-4 spectrofluorometer and FluorEssence software interface used to read fluorescence emission

For subsequent trials, the cuvette was switched from a 3 mL cuvette holding a 1 mL sample to a 1 mL cuvette to avoid any potential errors such as light scattering. The 1-AMA concentration was lowered from 2 to 1 μM for a third trial due to the results from the second trial.

3. RESULTS AND DISCUSSION

This chapter explains in detail the results obtained from the procedures that were described in the methodology section.

3.1 PRELIMINARY ANALYSIS

Results for the first part of the analysis, obtained from the odor data set received from Urban Site 1 (Figure 34), revealed that the year 2014 experienced the largest number of odor complaints (*n* = 98), with the most number of complaints logged in the month of September (*n* = 51); followed by December (*n* = 44) and February (*n* = 43). For Urban Site 2, the year with the highest number of odor complaints was 2005 (*n* = 76), followed by 2012 (*n* = 60) and 2013 (*n* = 55). For both sites, the large number of odor complaints in 2005, followed by 2012 and 2013, could be related to hurricane events, due to substantially greater amounts of waste received, and stored on the site with flooding in the area (Personal communication with site personnel), although over potential sources such as RSMs or Chinese drywall could not be ruled out.

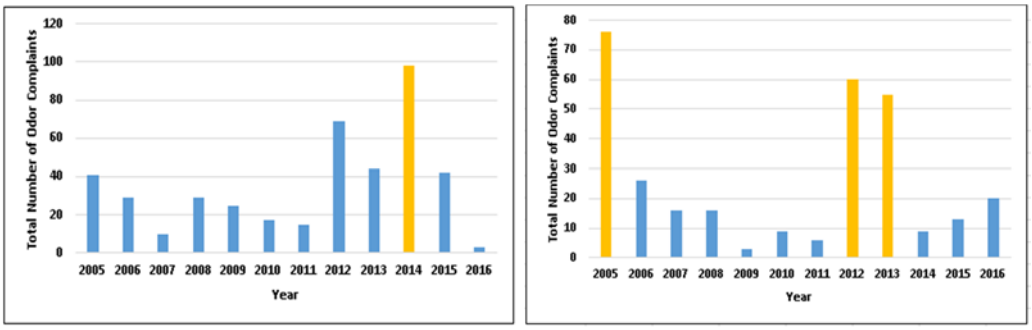

Figure 34. Incidence of odor complaints by year, July 2005 – March 2016 for Urban Site 1 (left) and January 2005-September 2016 for Urban Site 2 (right); note 2005 and 2016 data are incomplete and do not reflect the entire year

Frequency of odor complaints for Urban Site 1 showed that slightly more odor complaints occur during the dry season, from November until April (*n* = 225) versus the wet season (*n* = 196) (Figure 35). September has the highest total number of complaints for the time period (*n* = 51) with an average of 4.6 per month. Urban Site 2 had the highest frequency of complaints in July, with a total number of 60. The next highest months were January and November with a total of 39 and 32, respectively.

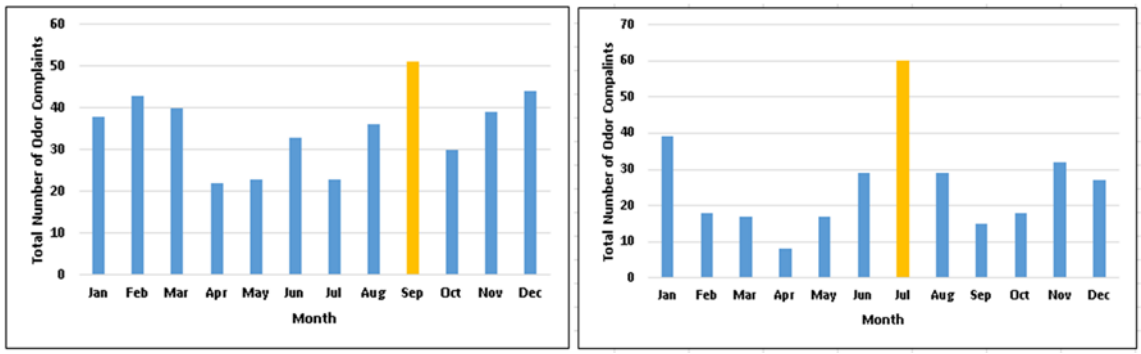

Figure 35. Incidence of odor complaints by month, July 2005 – March 2016 for Urban Site 1 (left) and January 2005-September 2016 for Urban Site 2 (right); note 2005 and 2016 data are incomplete and do not reflect the entire year

Working days of the week (Monday through Friday) had more odor complaints than the weekends, possibly because people were home more on the weekend and the olfactory impacts did not allow them to smell the odors, unlike evenings during the week where being away all day caused their olfactory processes to notice the odor more (Figure 36).

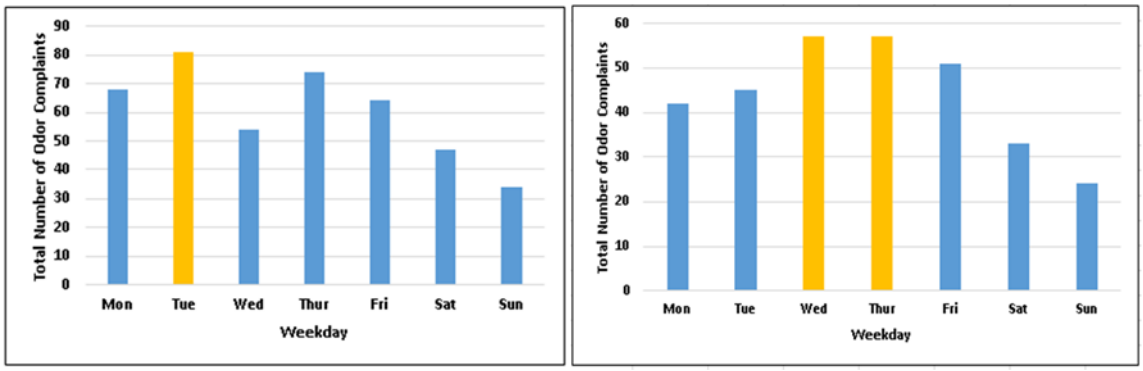

Figure 36. Incidence of odor complaints by day of the week, July 2005 – March 2016 for Urban Site 1 (left) and January 2005-September 2016 for Urban Site 2 (right); note 2005 and 2016 data are incomplete and do not reflect the entire year

Slightly more odor complaints were received in the afternoon hours (Urban Site 1: 52%, $n = 164$; Urban Site 2: 54%, $n = 142$) compared to the morning hours (Urban Site 1: 48%, $n = 150$; Urban Site 2: 44%, $n = 114$), which may be related to people coming home from work in the afternoon and spending more time at home rather than in the morning hours on the rush to work or school, but the frequency of occurrence is essentially the same.

The next step was to see how many days during the time period (2005 – 2016) had more than one odor compliant in the same day. Since the year 2016 had only three data points, it was excluded from further analysis, while the year 2005, even though it was also a year with partial data, had a larger range of dates (07/05/2005 – 12/28/2005) and a total of 41 odor complaints, so it was included in the analysis. Results at Urban Site 1 showed that the most odor complaints in the same day were in 2005, 2006, 2009 and from 2012-2015, while for Urban Site 2 similar years were recognized: 2005, 2006 and 2013 (Figure 37).

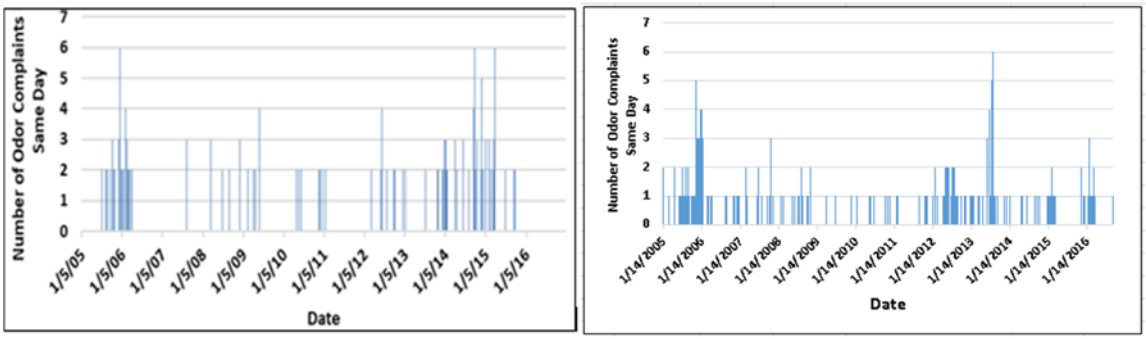

Figure 37. Dates with the most odor complaints recorded in the same day for July 2005 – March 2016 for Urban Site 1 (left) and January 2005-September 2016 for Urban Site 2 (right); note 2005 and 2016 data are incomplete and do not reflect the entire year

The most number of complaints were filed on December 9, 2005 with 6, and an additional 3 more were made on December 5 and 6 of that same year. February 2, 2006 had 4 odor complaints on the same day, while February 13, 2006 had 3 more of them. Year 2009 had 4 odor complaints in almost consecutive days, on May 26 and May 28, 2009. Year 2012 had 4 odor complaints on June 7, 2012. The most active year for reporting frequency on the same day was 2014 (Figure 38) with September 16, 18, and 19, 2014 having a total of 10 complaints filed altogether. According to the facility manager, this episode was due to the landfill operation (e.g. Class 1, Class 3, yard waste processing, compost operations and sludge pelletizer) towards the end of the dates noted, which all may have contributed to odors. Year 2015 also had elevated numbers of odor complaints in the same day throughout the whole year, with the largest number ($n = 6$) occurring on March 26, 2015. Odor complaints decreased after 2014, since Urban Site 1 changed the type of waste that it was receiving. They no longer had the organic fraction of the waste, since converting to 100% incineration (ash monofill) and stopping the practice of receiving recovered screen material (RSMs) containing high quantities of drywall (sulfur). This change in waste composition resulted in substantially lower frequency of odor complaints (from $n = 98$ in 2014 to $n = 42$ in 2015).

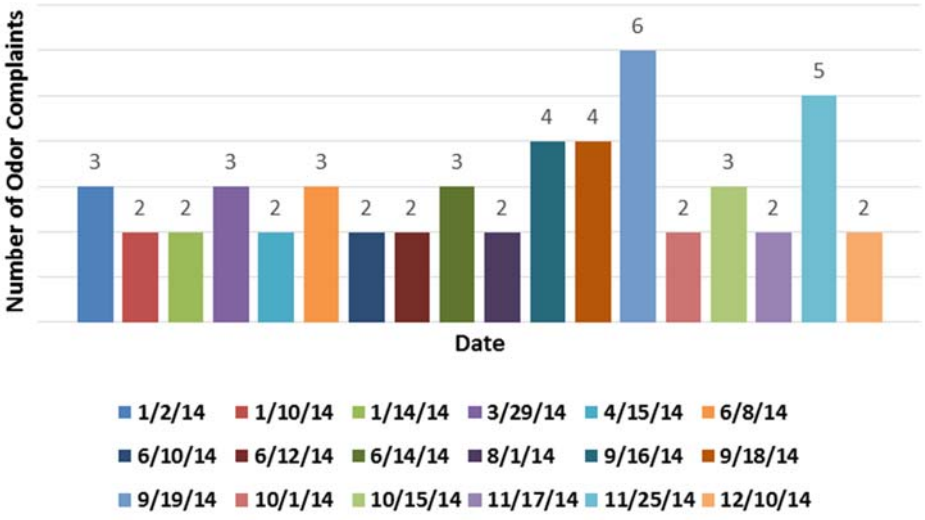

Figure 38. Odor complaints in the same day for 2014, Urban Site 1

Since three or more odor complaints in the same day trigger corrective action (Personal communication with site personnel), for further analysis, days with the largest number of complaints (6) in the same day were investigated. The year 2014 had three days in a row with a large number of complaints in the same day that could be related. Dates taken for analysis were: 12/09/05 (6 complaints), 09/16/14 (4 complaints); 09/18/14 (4 complaints); 09/19/14 (6 complaints) and 03/26/15 (6 complaints). When mapping the locations of the odor complaints received for each date, it was observed that the largest number of complaints is coming from the same neighborhood for all cases (Figure 39).

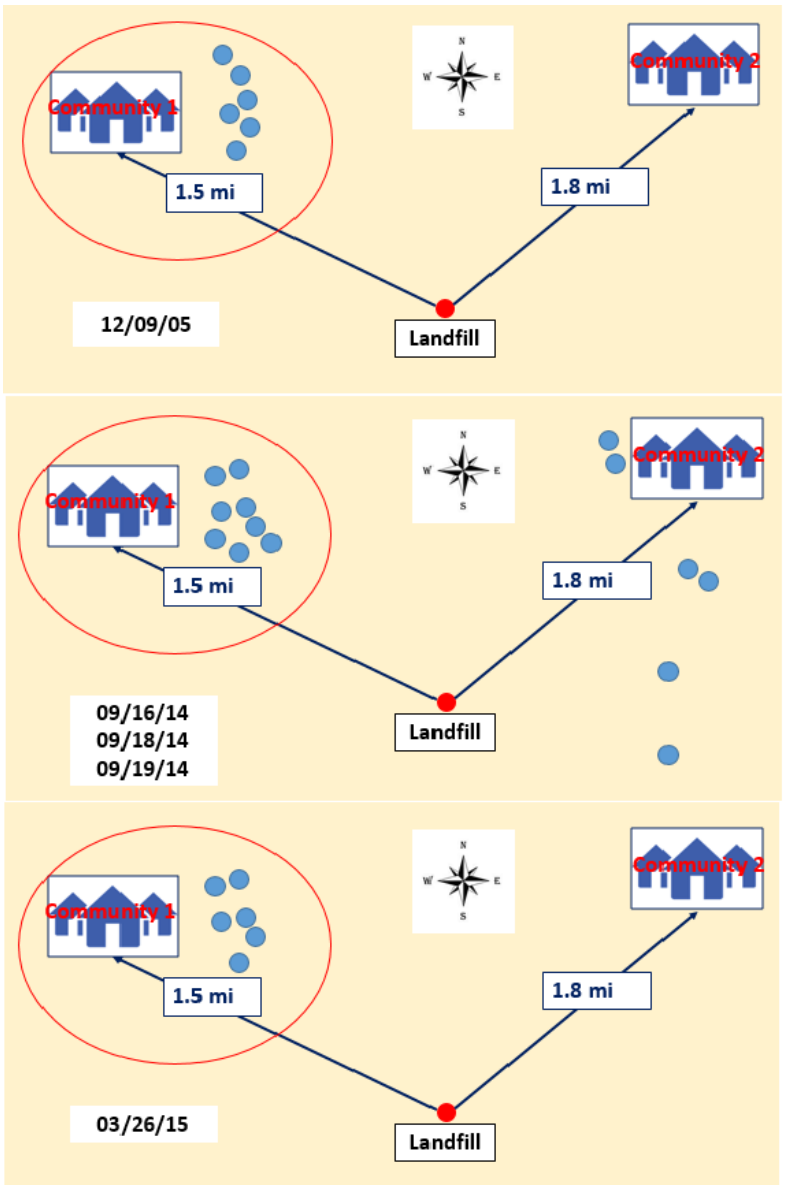

Figure 39. Clusters of Odor Complaints (Urban Site 1)

The next step was to examine the meteorological conditions at the time the odor complaint was received, as well as for the whole day. Meteorological conditions, in Table 24, showed a possibility for a correlation between odor complaints and weather conditions since for all cases, meteorological conditions were very similar. In all examined cases, the wind speed was weak,

the wind direction was south, temperature and pressure dropped from the previous day and there was no precipitation, while stable weather conditions were present (refer to Appendix B). Only in the case of September 19, 2014, according to weather station data, average wind direction was different (ENE), but the exact time of the odor complaint reported that the wind direction was also from the south.

Table 24. Summary of Meteorological Conditions at the Time the Odor Complaint Occurred for Urban Site 1 (Weather Underground)

Date	Number of Complaints	Rain, Inch	Wind Direction	Wind Speed, mph	Avg T, °F	Avg H, %	Avg P, Inch	Weather Condition
12/09/05	6	0.00	South, SSW	5.7	75.0	93.0	30.2	Partly cloudy
09/16/14	4	0.00	South, SSW	3.0	82.0	77.2	30.0	Mostly cloudy
09/18/14	4	0.00	South	10.6	83.3	73.6	29.9	Mostly cloudy
09/19/14	6	0.00	South	1.4	76.9	92.6	21.9	Mostly cloudy
03/26/15	6	0.11	South, WSW	6.5	75.7	83.2	30.0	Mostly cloudy

T = Temperature, H = Relative Humidity, P = Pressure

The second part of the preliminary analysis investigated the correlation between consistencies in values on the day complaints were filed when compared to the conditions the day before. Odor complaint data from both sites were used, and days with three or more complaints in the same day were retrieved. Urban Site 1 had total of 26 days with three or more complaints in the same day for the time frame of 2005 – 2016, while Urban Site 2 had a total of 17 days for the time period of 2005 – 2015. Meteorological parameters (temperature, humidity, pressure, wind direction and wind speed) were tested both for the day of the complaint as well as for the exact time when the complaint was filed and compared with the same conditions from the day before (Figure 40 – Figure 43).

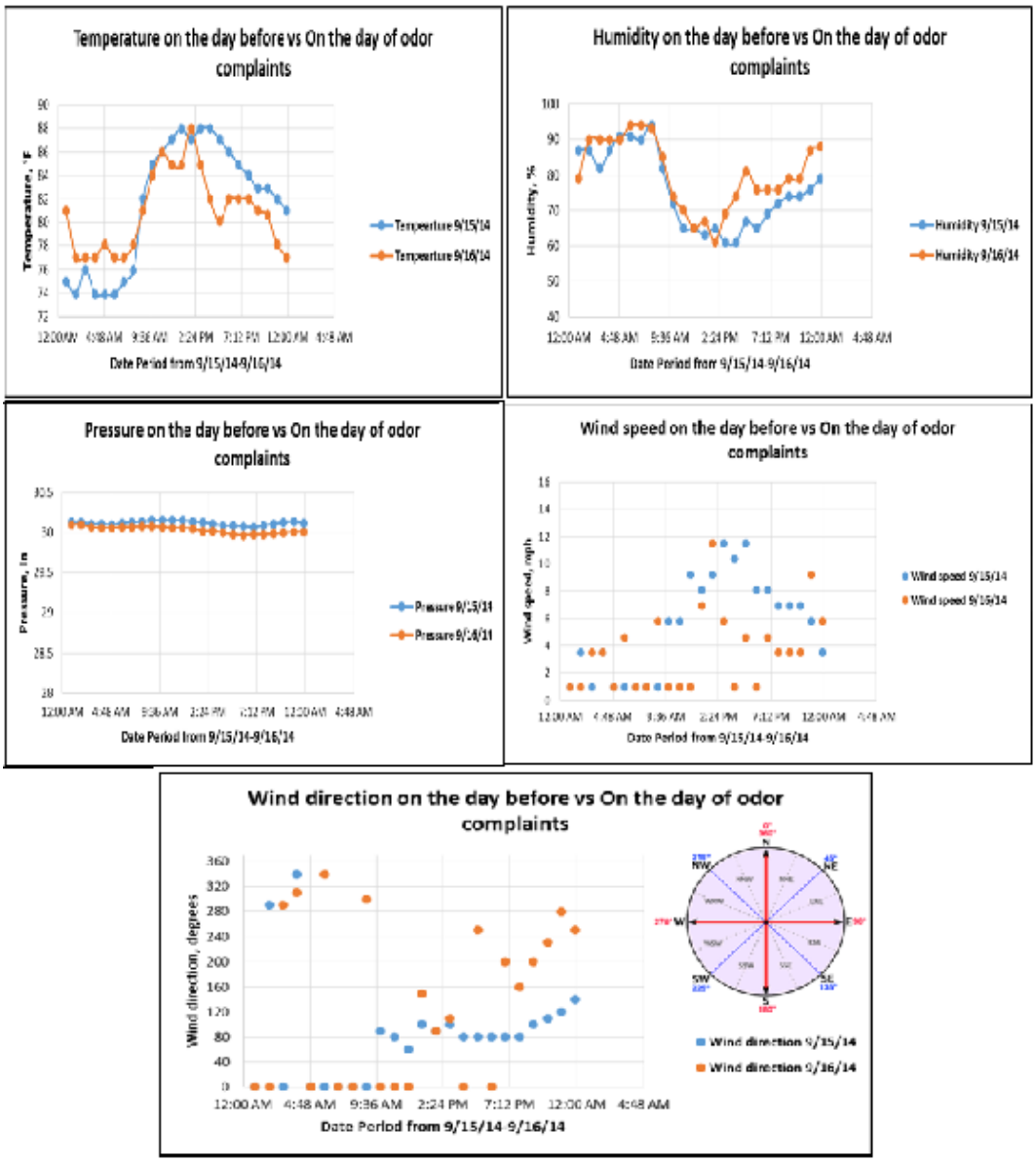

Figure 40. Meteorological Conditions: Temperature (Upper Left), Humidity (Upper Right), Pressure (Lower Left), Wind Speed (Lower Right) and Wind Direction (Bottom), for the Day the Complaint was filed on 09/16/14 vs. the Previous Day, Urban Site 1

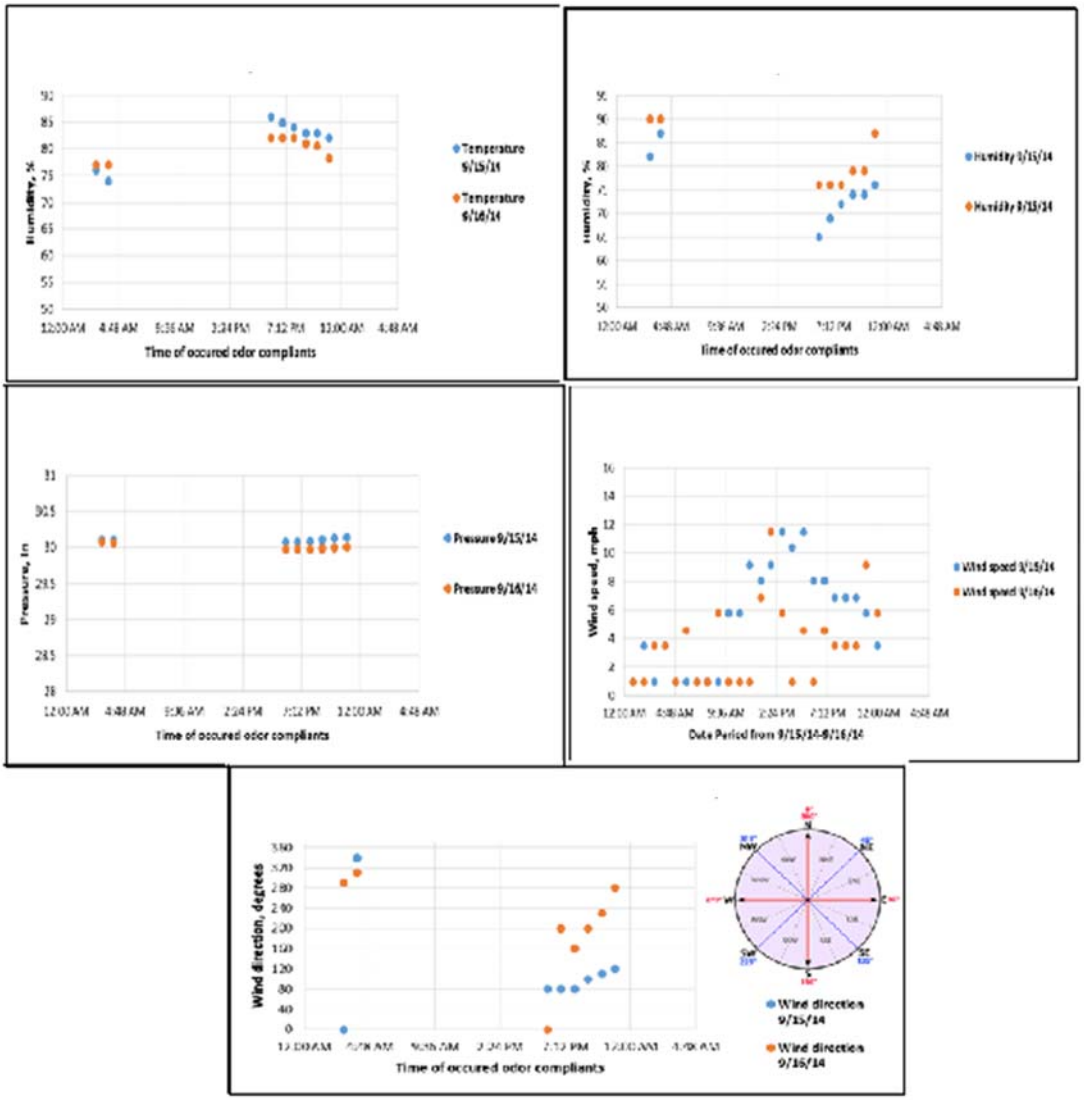

Figure 41. Meteorological Conditions: Temperature (Upper Left), Humidity (Upper Right), Pressure (Lower Left), Wind Speed (Lower Right) and Wind Direction (Bottom), at the Time the Complaint was Filed for 09/16/14 vs. the Previous Day, Urban Site 1

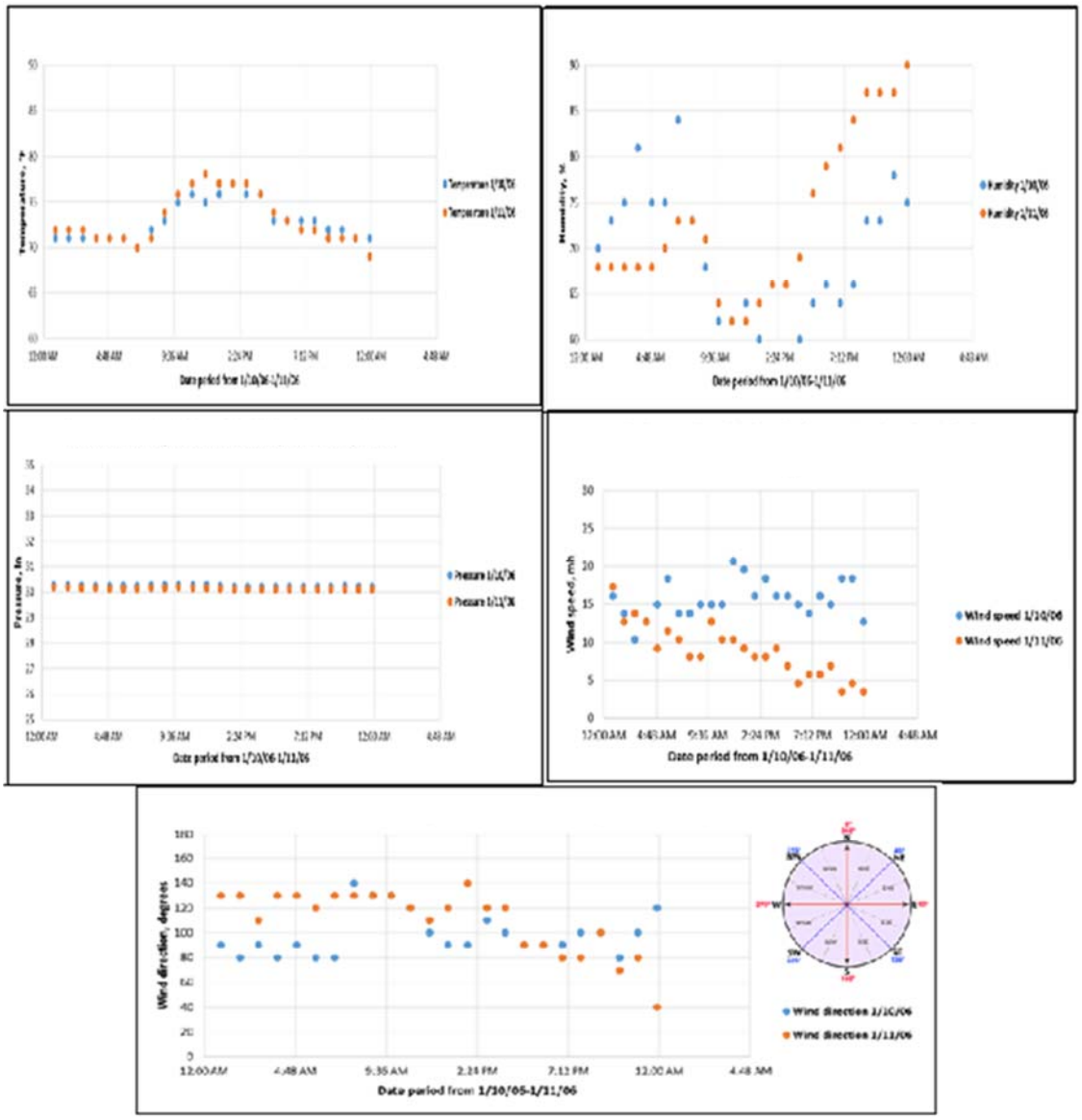

Figure 42. Meteorological Conditions: Temperature (Upper Left), Humidity (Upper Right), Pressure (Lower Left), Wind Speed (Lower Right) and Wind Direction (Bottom), for the Day the Complaint was filed on 01/11/06 vs. the Previous Day, Urban Site 2

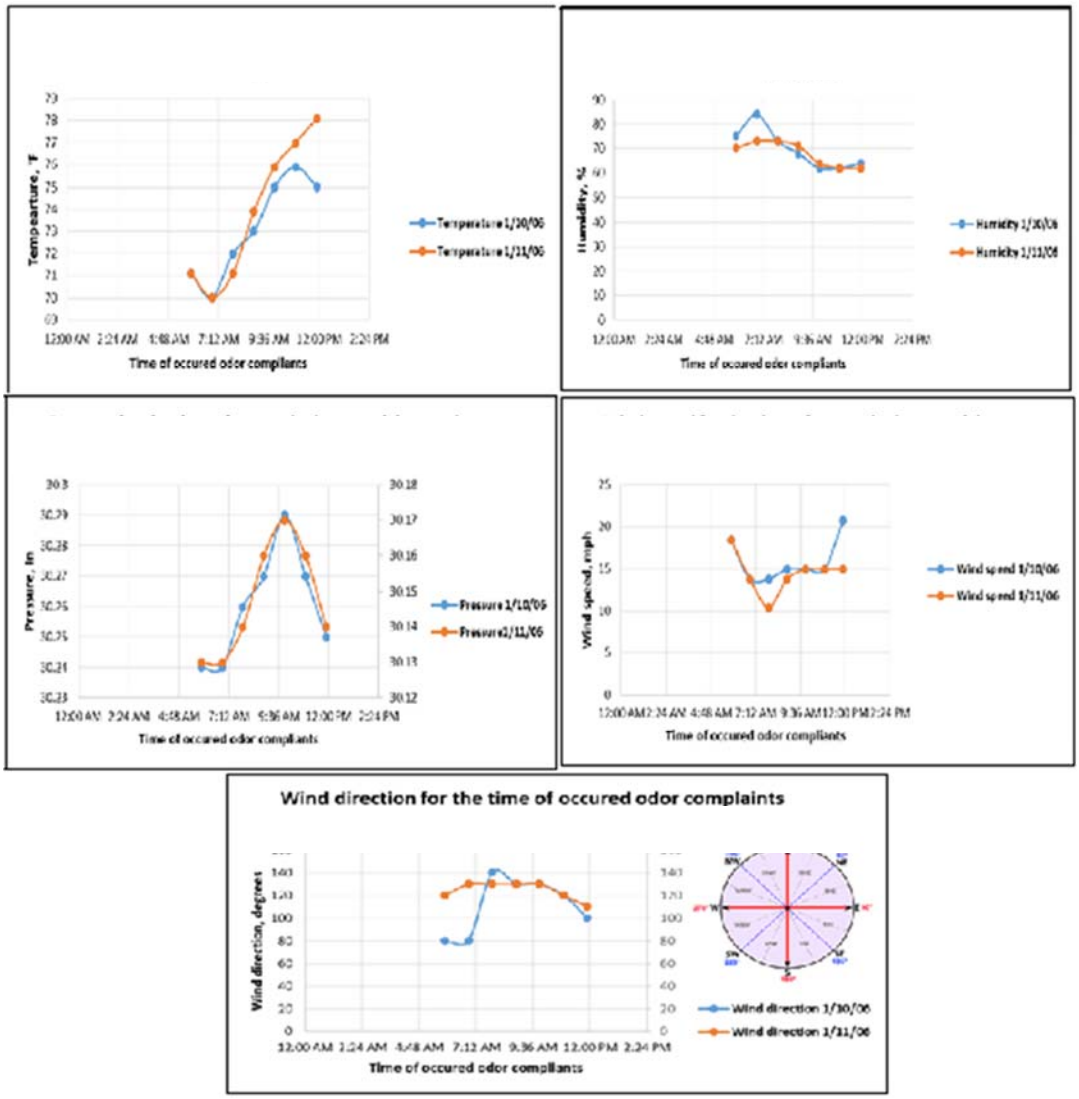

Figure 43. Meteorological Conditions: Temperature (Upper Left), Humidity (Upper Right), Pressure (Lower Left), Wind Speed (Lower Right) and Wind Direction (Bottom), at the Time the Complaint was Filed for 01/11/06, Urban Site 2

Table 25 summarizes the statistical correlation testing for both conditions. Wind direction and wind speed have the lowest correlations when compared to the values from the day before, which is expected since those have the largest variability (Sakawi et al. 2011), while temperature, humidity, and pressure had consistently stronger correlations because they tend to be relatively constant within a narrow range for South Florida (Climate Data-Florida 2017).

Table 25. Correlations of Meteorological Parameters at the Time the Complaint Occurred v. the Entire Day

Site	Temperature		Humidity		Pressure		Wind Speed		Wind Direction	
	Exact Time	Whole Day	Exact Time	Whole Day	Exact Time	Whole Day	Exact Time	Whole Day	Exact Time	Whole Day
09/16/14 Urban Site 1	0.91	0.81	0.90	0.88	0.43	0.68	-0.09	0.27	0.34	0.15
01/11/06 Urban Site 2	0.96	0.93	0.84	0.36	0.97	0.94	0.29	-0.18	0.39	0.02

Also, correlations between temperature and humidity, temperature and pressure, and humidity and pressure were tested (Figure 44).

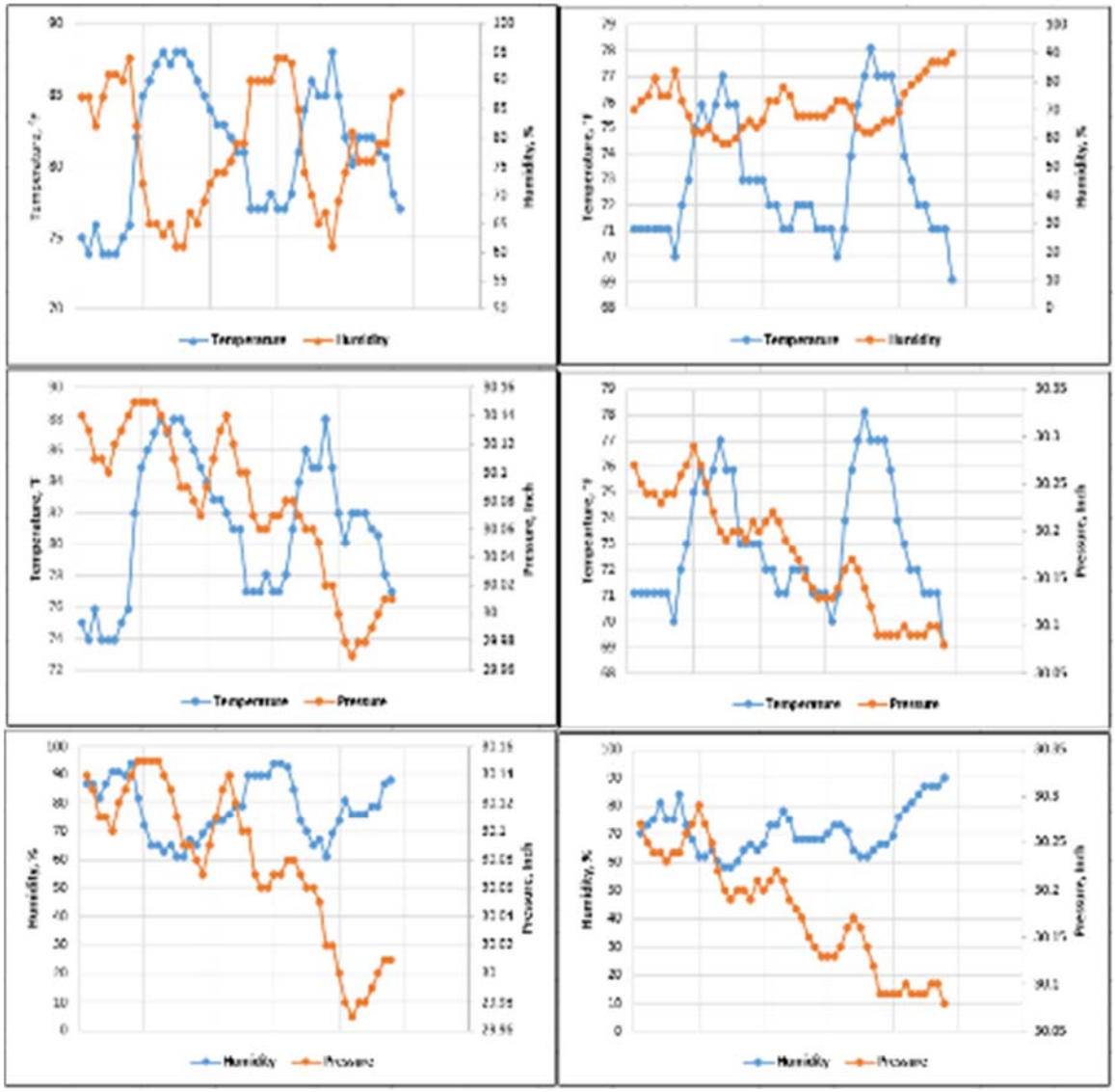

Figure 44. Relationship between Temperature, Humidity and Pressure, 09/16/2014 Urban Site 1 (left) and 01/11/2006 Urban Site 2 (right)

Results showed that strongest relationship was between temperature and humidity, which was negatively correlated (Urban Site 1: r = -0.94; Urban Site 2: r = -0.73) (Table 26). No relationship was noticed between temperature and pressure.

Table 26. Correlation coefficients between meteorological parameters for both sites

	Temperature		Humidity		Pressure	
	09/16/14 Urban Site 1	01/11/04 Urban Site 2	09/16/14 Urban Site 1	01/11/04 Urban Site 2	09/16/14 Urban Site 1	01/11/04 Urban Site 2
Temperature	1	1	-0.94	-0.73	-0.02	-0.04
Humidity	-0.94	-0.73	1	1	-0.01	-0.34
Pressure	-0.02	-0.04	-0.01	-0.34	1	1

3.2 ANALYSIS OF ISOLATED ODOR COMPLAINTS

Frequency of odor complaints was compared to the average value of temperature, humidity, pressure, wind speed and rainfall for each day when three or more complaints were received in the same day. Results presented in Table 27 show that there is an absence of a strong correlation between frequency of odor complaints and meteorological conditions. No data was available for precipitation accumulation from the nearest weather station located to Urban Site 2, so it was excluded from further analysis. Since the next closest weather stations were much further away, it was decided that the differences would be too great compared to the location of interest, so data from the next nearest weather station was not considered.

Table 27. Correlation for Urban Site 1 and Urban Site 2 with Temperature, Humidity, Pressure, Wind Speed and Precipitation Accumulation (only for Urban Site 1)

	Avg Temperature	Average Humidity	Average Pressure	Average Wind Speed	Precipitation Accumulation
Urban Site 1	0.24	0.37	-0.30	<-0.01	0.05
Urban Site 2	0.12	0.17	-0.21	-0.19	N/A

Dividing the data set into dry season (November until April) and wet season (May until October) obtained the same result for Urban Site 1 in that no correlation was detected between the number of odor complaints and meteorological parameters (Table 28). Results obtained for Urban Site 2 showed that the parameter that had the greatest influence on odor complaints was pressure. Furthermore, a higher number of odor complaints consistently occurred during the dry season, for both sites, and one of the factors that could potentially influence such events, for Urban Site 2, could be pressure drop (Sadowska-Rociek et al. 2009).

Table 28. Correlations of Meteorological Parameters for Urban Site 1 and Urban Site 2 based on the Wet and Dry Season

	Urban Site 1		Urban Site 2	
	Wet Season	Dry Season	Wet Season	Dry Season
Number of Complaints	$n = 40$	$n = 42$	$n = 15$	$n = 27$
Avg Temperature	0.20	0.26	-0.66	0.36

	Urban Site 1		Urban Site 2	
	Wet Season	Dry Season	Wet Season	Dry Season
Average Humidity	0.52	0.24	-0.07	0.15
Average Pressure	-0.34	-0.29	0.68	-0.73
Average Wind Speed	-0.29	0.31	-0.37	0.03
Precipitation Accumulation	0.13	-0.23	0.13	N/A

Precipitation accumulation data was analyzed based on the previous 24 hours, 3 days before and 7 days before the day when three or more odor complaints occurred in the same day. This analysis showed no correlation between the frequency of odor complaints and the amount of precipitation measured for Urban Site 1. Results for Urban Site 2 showed that the number of odor complaints could be related to the amount of precipitation that has been accumulated three days prior to the odor complaint. Results are presented in Table 29. Different results from two separate sites could indicate how odor complaints are occurring randomly and attempting to analyze only one scenario in which they could potentially occur might be an oversimplification of a complex phenomenon.

Table 29. Correlation for Urban Site 1 and Urban Site 2 with 24h, 3 days before and 7 days Precipitation Accumulation before the Odor Complaint

Parameters	Urban Site 1	Urban Site 2
Number of Complaints	$n = 101$	$n = 62$
24 hours	0.16	0.65
3 days	0.10	0.75
7 days	0.10	0.58

Rainfall data collected for 24 hours, 3 days and 7 days prior to an odor episode was analyzed for Urban Site 1 and Urban Site 2, and dates that differed from the rest of the sample were identified. The rainfall distribution for Urban Site 1 revealed three dates (05/26/2009; 05/28/2009 and 06/14/2014) with rainfall amounts different than the rest of the dates considered. Months identified for further analysis were May 2009 and June 2014. Historical data of 10 years for May (1999-2009) and June (2004-2014) were tested for normal distribution by creating Q-Q normal probability plot. Results revealed that in the case of May, the data set differs slightly from but generally approximates a normal distribution, while in the case of June, the data set is normally distributed. No outliers were identified for the month of June (time period 2004-2014). Analysis of historical data of 10 years prior (1999-2009) revealed that May 2009 (Figure 45) could be recognized as an outlier. Since the upper outer fence was calculated to be 15.14, the observation of 15.70 inches of rainfall (May 2009) is categorized as an “extreme outlier.”

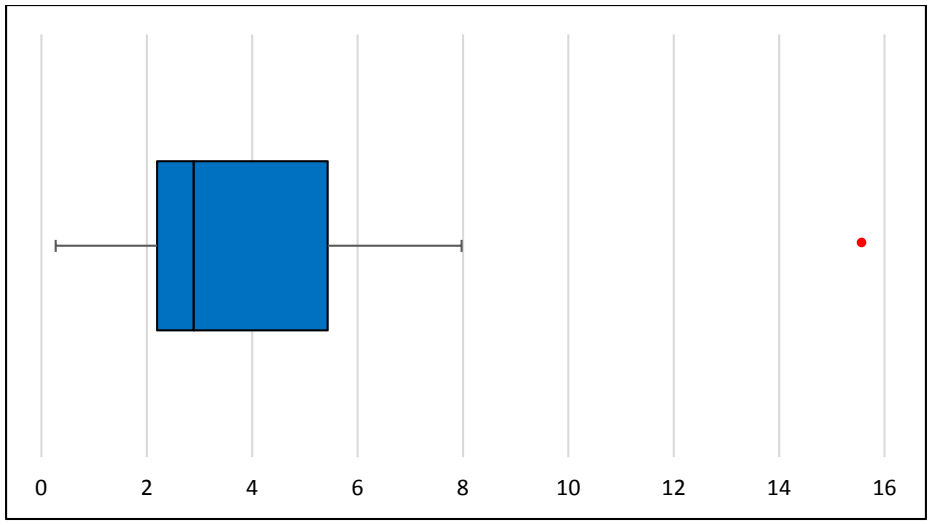

Figure 45. Identifying May of 2009 as an "Extreme Outlier" with Rainfall Accumulation of 15.70 Inches (Urban Site 1)

The month of May 2009 (circled), received 70% greater amount of rain when compared to the average value for the previous ten years (1999-2009), shown in Figure 46. In those ten years, for the month of May, the average rain accumulation was 4.75 inches, while May of 2009 recorded a total of 15.70 inches of rain. This finding is corroborated by the report of the National Weather Service (NOAA 2017), which identified May of 2009, in the location of Urban Site 1, as the second wettest May on record (with 15.69 inches). It is also important to note that the amount of 15.69 inches fell in just 14 days (May 18 to May 31).

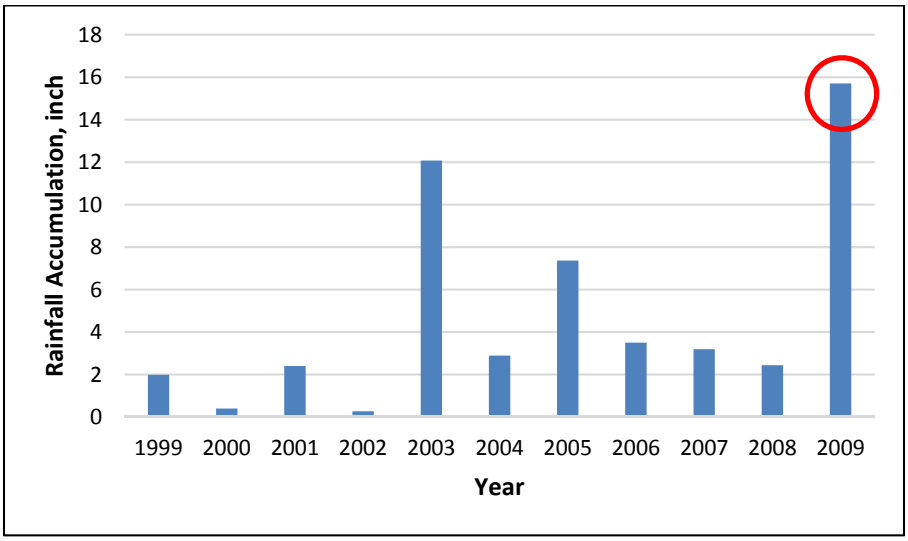

Figure 46. Total Monthly Rainfall Accumulation for Month of May, Time Period from 1999-2009 (Urban Site 1)

3.3 ANALYSIS OF DATES WITH NO ODOR COMPLAINTS

Since there were too few data points to show a positive relationship between dates with multiple odor complaints and meteorological conditions, the inverse (dates with no odor complaints filed) was investigated to find out if the days with three or more complaints in the same day are distinguishable when compared to the dates when complaints have not been recorded. Nonetheless, no relationship between the absence of odor complaints and meteorological conditions was revealed for Urban Site 1 or 2 (Table 30).

Table 30. Correlation for Urban Site 1 and Urban Site 2 with Additional Data from Days with No Complaints

Parameters	Urban Site 1	Urban Site 2
Time Frame	07/02/05 – 03/18/16	01/11/05 – 09/14/16
Dates without Odor Complaints	n = 3912	n = 4258
Number of Complaints	n = 478	n = 309
Average Temperature	0.05	0.03
Average Humidity	0.08	0.09
Average Pressure	-0.06	<0.01
Average Wind Speed	-0.09	-0.03
Precipitation Accumulation	0.02	0.05

Results from comparing wet and dry seasons for both sites revealed that Urban Site 2 had more odor complaints (n = 168) in the wet season compared to Urban Site 1, which had slightly more odor complaints in the dry season (n = 246). The largest variations were related to humidity and temperature when compared to the average value (Table 31). This is expected because temperature and humidity are related with each other, since changes in temperature create changes in humidity of the ambient air (Linden 2013).

Table 31. Comparison of Dry and Wet Season for Urban Site 1 and Urban Site 2 with Additional Data with No Complaints

Parameters	Urban Site 1		Urban Site 2	
	Dry Season	**Wet Season**	**Dry Season**	**Wet Season**
Dates without Odor Complaints	n = 1951	n = 1961	n = 2101	n = 2157
Number of Complaints	n = 246	n = 232	n = 140	n = 168
Average Temperature	70.9 ± 7.2	81.8 ± 3.5	71.3 ± 6.8	81.2 ± 4.5
Average Humidity	69.1 ± 9.2	72.9 ± 6.8	70.3 ± 10.8	73.8 ± 8.2
Average Pressure	30.1 ± 0.1	30.0 ± 0.1	30.1 ± 0.1	30.0 ± 0.7
Average Wind Speed	9.9 ± 3.5	8.3 ± 3.4	9.8 ± 3.6	8.0 ± 3.6
Precipitation Accumulation	194.6 ± 0.4	441.1 ± 0.2	192.2 ± 0.4	370.3 ± 0.5

It is interesting to note that in both cases (Urban Site 1 and Urban Site 2), meteorological conditions were similar. Also, it was observed that more stable weather conditions tend to occur in the dry season, while in the wet season, there was more frequent rain and thunderstorm events.

For both sites, conditions observed during the dry season were: lower rainfall, slightly stronger winds, lower humidity and temperature, and higher pressure when compared to the wet season.

Autocorrelation analysis of odor complaint frequencies revealed that previous day complaint records were not good predictors of the following day's citizen reported odor annoyances. Autocorrelation analysis revealed the lag 1 day correlation was 0.11 for Urban Site 1 and 0.23 for Urban Site 2. Lag 2 and 3 for both sites showed even lower correlations: for lag 2 the values were 0.08 and 0.16 for Urban Site 1 and Urban Site 2, repetitively. Lag 3 correlations were 0.05 for the Urban Site 1 and 0.10 for the Urban Site 2. Results indicated no potential for predicting the number of odor complaints from one day to the next.

3.4 ANALYSIS OF ISOLATED DAYS AND RANDOM DAYS WITH NO COMPLAINTS WITH SIMILAR WEATHER PATTERNS

Summary statistics revealed that the mean values for the meteorological parameters (temperature, humidity, pressure, wind speed and precipitation accumulation), both for the days when complaints occurred as well as for the days without complaints, were very similar (>95%), except for precipitation accumulation (Table 32). Results revealed that the tendency of odor complaints could be related to slightly higher temperature and humidity with lower pressure and windy days. Also, higher precipitation accumulation was noticed for the days when odor complaints occurred and that was a parameter that showed the highest difference when compared to days without odor complaints.

Table 32. Similarity between Mean Values of Weather Conditions for Days with Complaints vs. Days Without Complaints

Parameter	Urban Site 1	Urban Site 2
Temperature	99.8%	98.8%
Humidity	99.5%	99.3%
Pressure	100%	99.9%
Wind speed	94.8%	95.3%
Precipitation accumulation	58.3%	46.5%

Days with three or more complaints in the same day were compared with the same number of days selected at random from days with no odor complaints but very similar meteorological conditions. For each of those days, meteorological data was collected for the previous day. The aim of this analysis was to distinguish weather patterns when complaints occur compared to the days when complaints were not received. Results revealed that on average around 61% of the differences between meteorological conditions had the same trend, both when the complaint occurred and when no complaint was filed, for Urban Site 1. For Urban Site 2, the average value of the same trend was 40%. Meteorological parameters that had the highest percent of the same trend in both scenarios were temperature with 67% and humidity with 78% for Urban Site 1, while for Urban Site 2, those were precipitation accumulation with almost 50% and temperature and pressure with 41% (Table 33).

Table 33. Percentage of Days with Similar Weather Trends (Complaint and Noncomplaint) for Urban Site 1 and Urban Site 2

Parameter	Urban Site 1	Urban Site 2
n	54	34
Temperature	67%	41%
Humidity	78%	35%
Pressure	52%	41%
Wind speed	48%	35%
Precipitation accumulation	59%	47%

It is interesting to note, that for Urban Site 1, it was more likely that the weather conditions were similar the day before (greater than 50% chance), but for Urban Site 2, the weather conditions were not similar the day before (less than 50% chance). Results for each individual weather parameter are presented in Figure 47 and Figure 48, and no obvious correlation in difference from the day before in terms of meteorological conditions can be observed, both with or without odor complaints, which results in an inability to identify a specific weather pattern that could potentially lead to predicting odor annoyances in these data sets. For example, in Figure 47 top left, the temperature difference for the days with complaints and the temperature difference for the days without complaints are both moving in the same direction (first two bars looking down), while we expected to see that they move in opposite directions if it was showing a way to distinguish the situation contributing to making a complaint. The percentage of 67% in Table 33reflects the frequency of both bars moving in the same direction. The differences between the two sites is likely related to the lower amount of data for Urban Site 2, since Urban Site 2 had only 17 days with 3 or more complaints in the same day, while Urban Site 1 had 27.

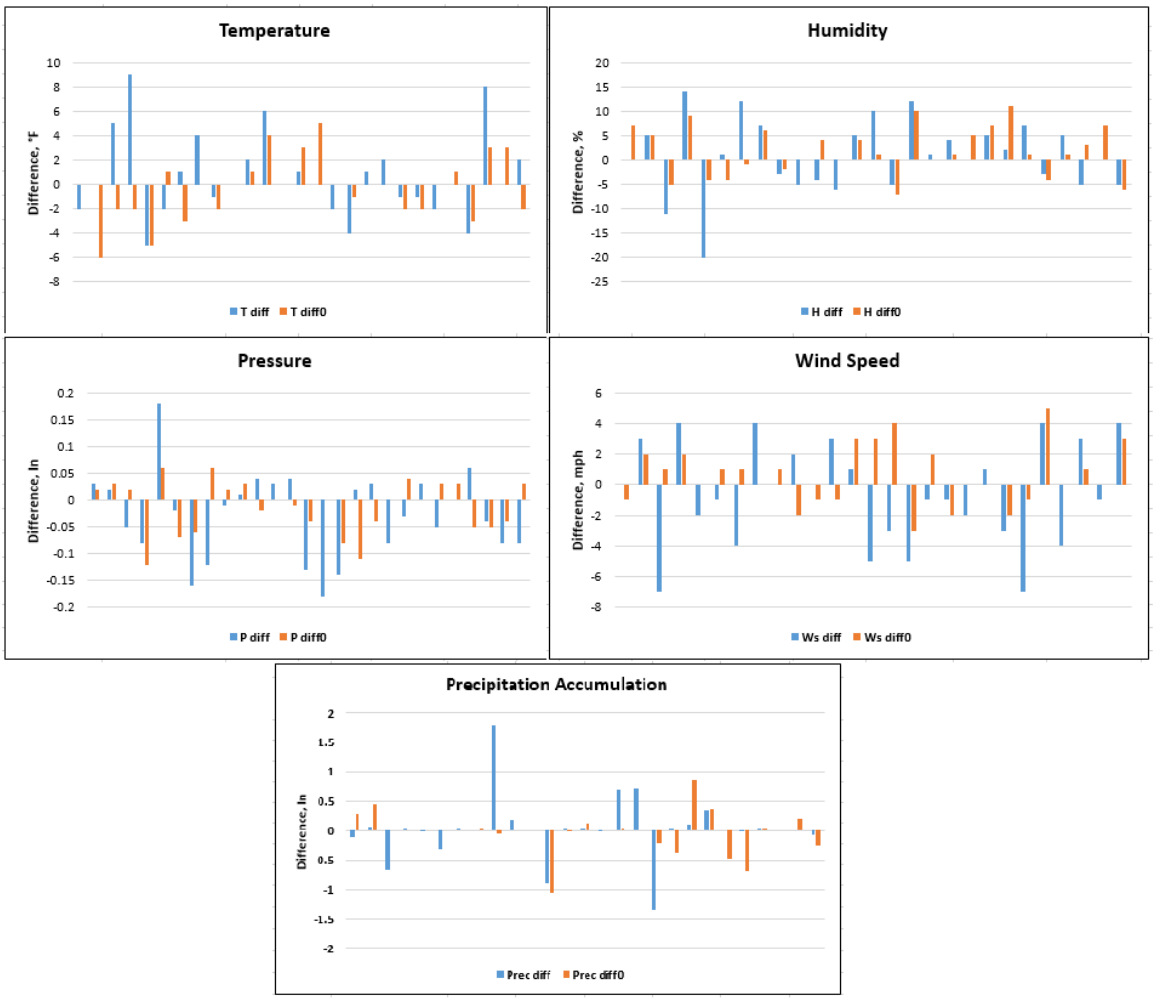

Figure 47. Differences in Meteorological Conditions: Temperature (Upper Left), Humidity (Upper Right), Pressure (Lower Left), Wind Speed (Lower Right) and Precipitation Accumulation (Bottom), with and without Odor Complaints: Urban Site 1

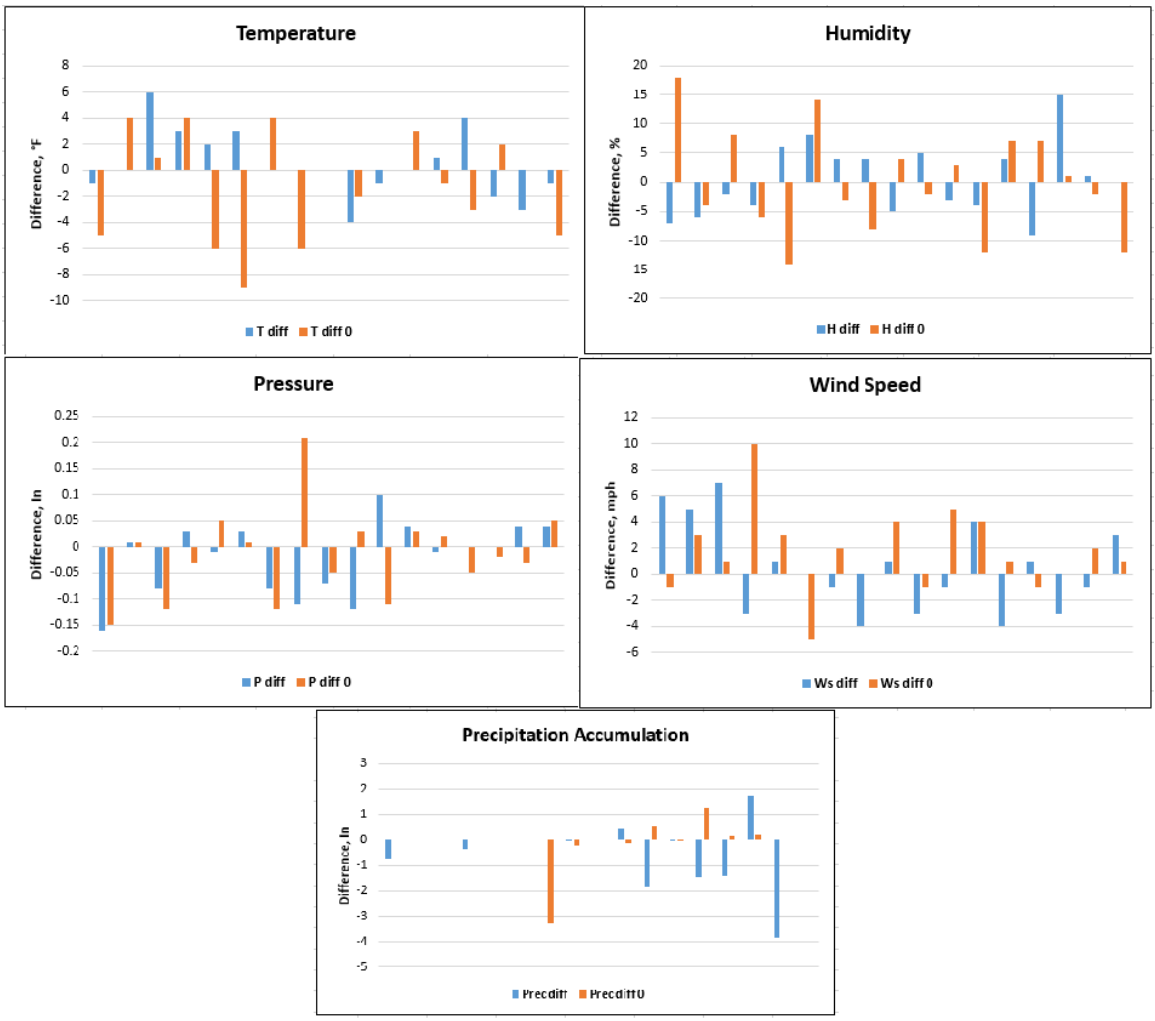

Figure 48. Differences in Meteorological Conditions: Temperature (Upper Left), Humidity (Upper Right), Pressure (Lower Left), Wind Speed (Lower Right) and Precipitation Accumulation (Bottom), with and without Odor Complaints: Urban Site 2

Analysis of wind direction and wind speed revealed which winds and at which speeds were the most frequent on the days when odor complaints occurred as well as for the days when there was an absence of same, for both Urban Site 1 and Urban Site 2. As previously stated in the site descriptions (2.1.1 and 2.1.2), the location of Urban Site 1 has predominant wind directions of south and east, while Urban Site 2 has predominantly easterly winds. Clusters of odor complaints confirmed the influence of the predominant wind directions since the greatest number of odor complaints occurred in the same locations. Clusters of odor complaints for Urban Site 1 were already presented in Figure 27 (3.1 Preliminary Analysis), while the clusters for Urban Site 2 are presented in Figure 49.

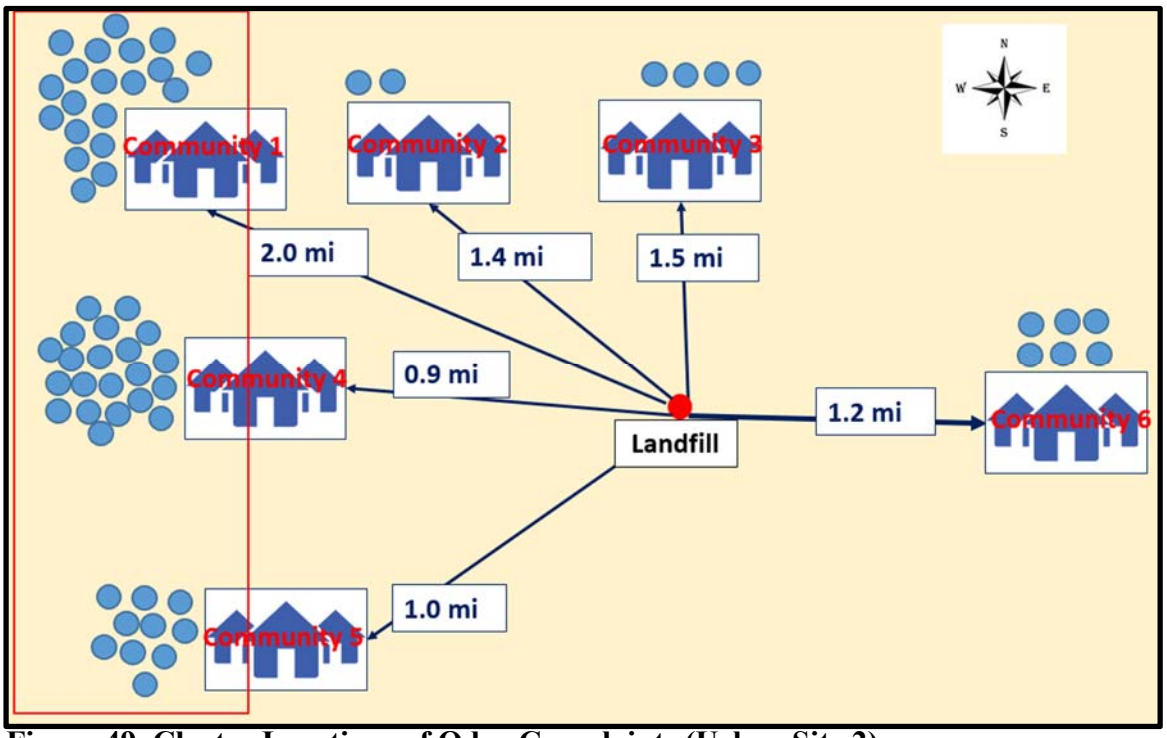

Figure 49. Cluster Locations of Odor Complaints (Urban Site 2)

For Urban Site 1, on the days when odor complaints occurred, the most frequent wind directions were SSE and South, or there was no wind, and for the random days with similar meteorological conditions but no odor complaints, the most frequent winds were East, SE, ESE, and the presence of very calm wind or no wind (Figure 50 and Figure 51). The most frequent wind speed range in both scenarios was from 8 – 12 mph, and the second highest was from 4 – 7 mph (Figure 54).

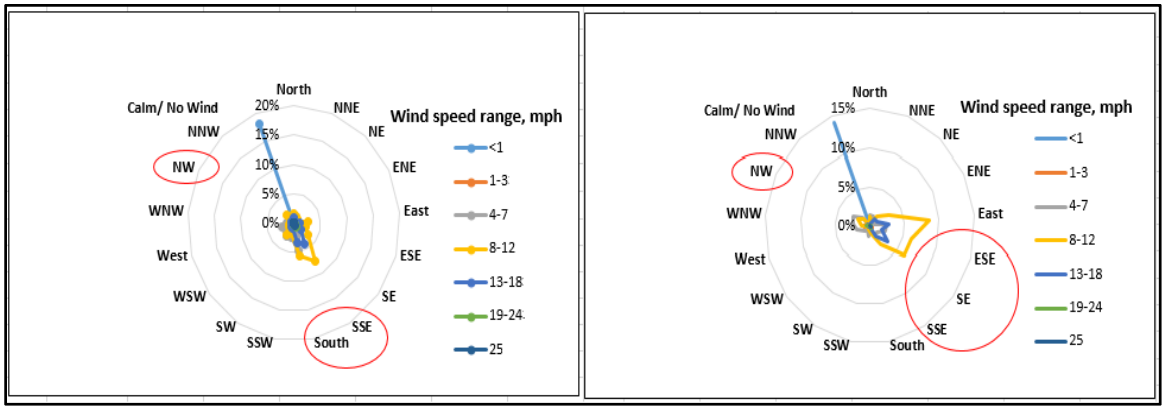

Figure 50. Urban Site 1 Wind Rose for the Days with Odor Complaints (left) and without Odor Complaints (right)

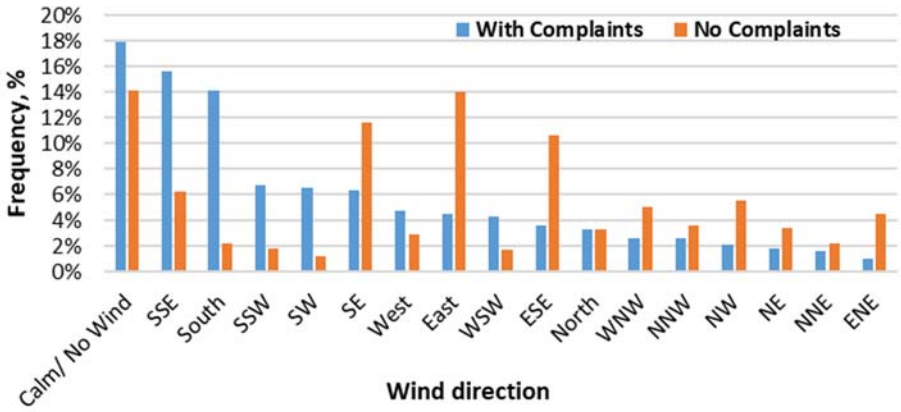

Figure 51. Most Frequent Wind Directions, with or without Odor Complaints, Urban Site 1

Urban Site 2 showed a similar relationship. In the scenario with odor complaints, the most frequent wind directions were ESE, SE or no wind, while for the second scenario in the absence of odor complaints, the most frequent wind directions were East, ESE, SE and SSE (Figure 52 and Figure 53). The range with most frequent wind speeds was from 8 – 12 mph, while the second highest was 13 – 18 mph (Figure 54).

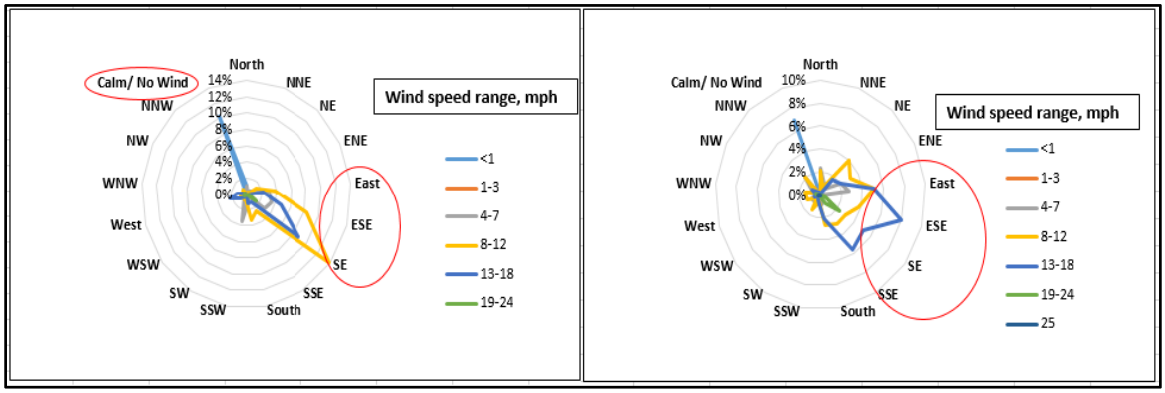

Figure 52. Urban Site 2 Wind Rose for the Days with Odor Complaints (left) and without Odor Complaints (right)

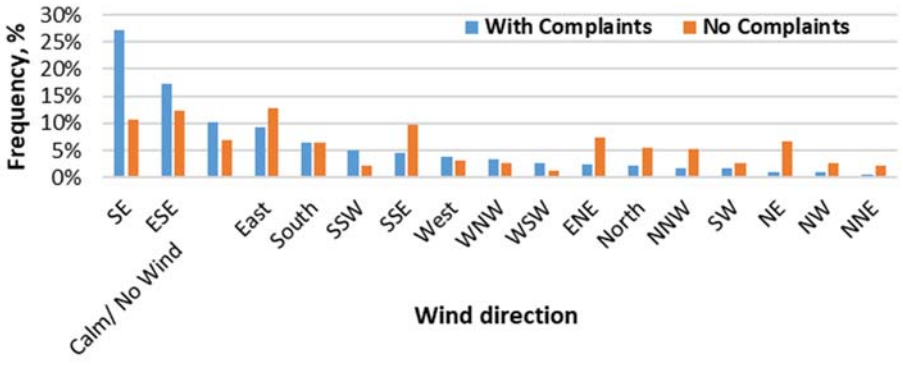

Figure 53. Most Frequent Wind Directions, with or without Odor Complaints, Urban Site 2

Notably in the case for both sites, the wind directions were very similar when odor complaints occurred as well as when complaints were not received. The strength of winds was the same in both scenarios, as well (Figure 54).

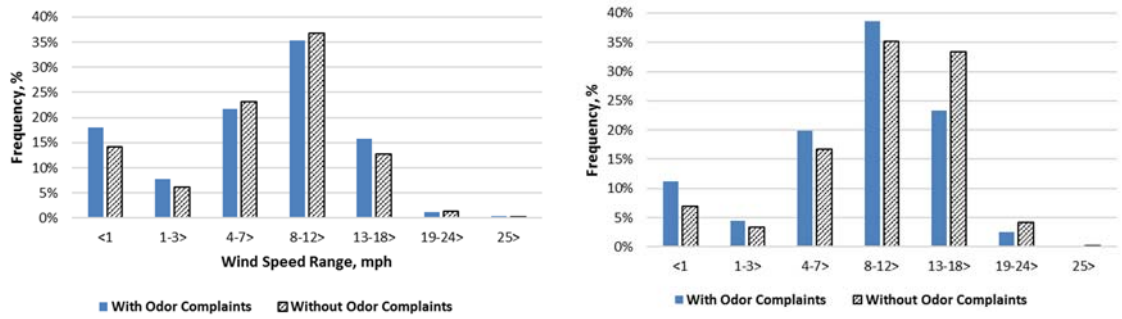

Figure 54. Most Frequent Wind Speeds, with or without Odor Complaints (left, Urban Site 1 and right, Urban Site 2)

Weather conditions and the most frequent events for both scenarios revealed that, in the case for Urban Site 1, mostly cloudy sky conditions prevailed on the days when odor complaints occurred, while scattered clouds were more prevalent when odor complaints were not received (Figure 55 and Figure 56).

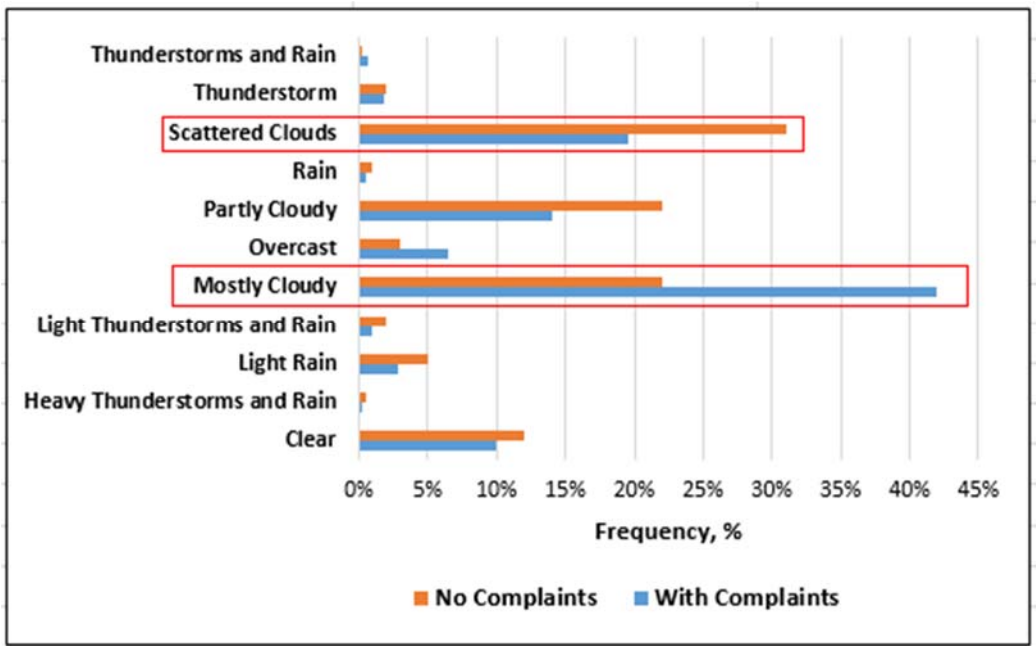

Figure 55. Frequency of Weather Condition Noted for Urban Site 1, with or without Odor Complaints

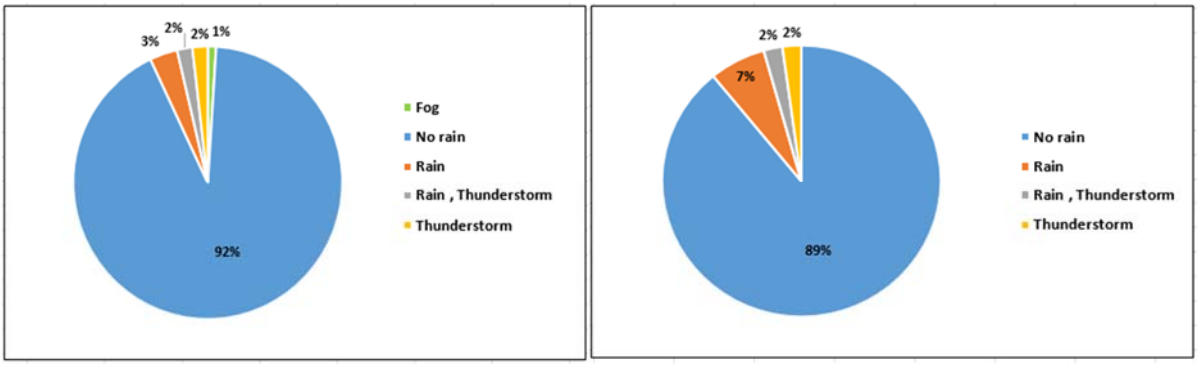

Figure 56. Frequency of Events for Urban Site 1: Days with Odor Complaints (left) and without Odor Complaints (right)

In the case of Urban Site 2, it was opposite situation. On the days when odor complaints were received, clear sky conditions prevailed, while on the days without complaints, mostly cloudy skies were most common (Figure 57). In the case of most frequent events, both sites had the same trend. On days with or without odor complaints, the most frequent event identified was presence of no events or no rain (Figure 58). Also, it was noticed that on the days when there was an absence of complaints, the rain was more frequent.

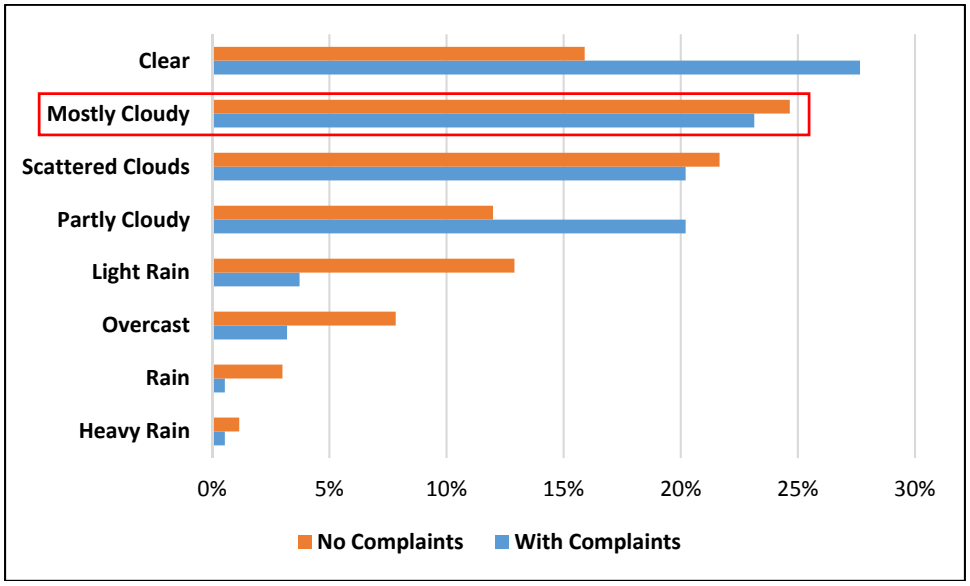

Figure 57. Frequency of Weather Condition Noted for Urban Site 2, with or without Odor Complaints

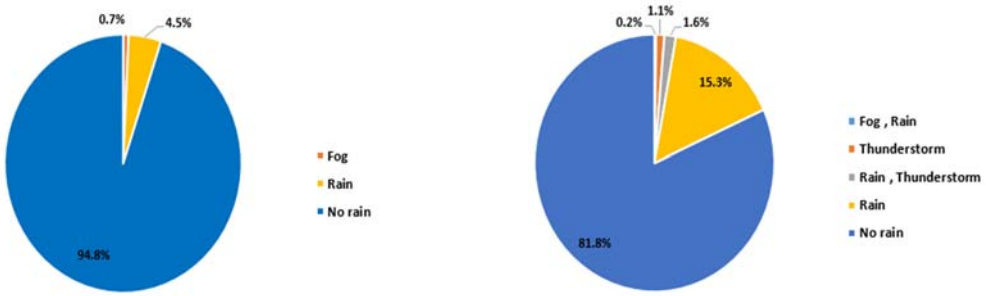

Figure 58. Frequency of Events for Urban Site 2: Days with Odor Complaints (left) and without Odor Complaints (right)

3.5 STATISTICAL ANALYSES CORRELATION MATRIX, PRINCIPAL COMPONENT ANALYSIS (PCA) AND LINEAR REGRESSION

A correlation matrix was used to test dependency among various meteorological variables and odor complaints from the solid waste sites. With so many variables, the table was reduced to reflect those impacts on the number of complaints. Table 34 represents the correlation matrix produced by XLStat®. The bold values meet the $p<0.05$ test, but none of the correlations could be defined as "strong." (greater than 0.7). The full matrix showed relationships between heat, wind, humidity and pressure on a given day, and some relationships between those variables but none with the number of complaints on a given day, nor with weather patterns on prior days. In part, this may be because so many days experienced zero complaints.

Table 34. Relationship between Frequency of Odor Complaints and Parameters of Interest Correlation Matrix

Variables	No of Complaints
Days -1	0.112
Days -2	0.081
Days -3	0.052
Temp High	0.053
Temp Chg	0.051
Temp Avg	0.045
Temp Low	0.034
Hum High	0.063
Hum Chg	**0.022***
Hum Avg	0.081
Hum Low	0.070
P High	-0.058
P Avg	-0.055
P Low	-0.058
Wind Speed Avg	**0.005***
Wind Speed Low	-0.086
Precip	**0.021***

*Statistically Significant ($p<0.05$)

PCA is designed to take a large number of variables, and use the eigenvalues that measure variability to create new factors. A Scree plot is sued to determine how many factors contribute significantly to the overall variance. Figure 59 is a Scree plot for the meteorological data as relevant to the number of odor complaints. It shows that the first 7 factors are greater than 1 and it takes 12 to account to 70% of the variance. This suggested that the odor complaints are random since no limited number of factors accounts for the majority of the variance.

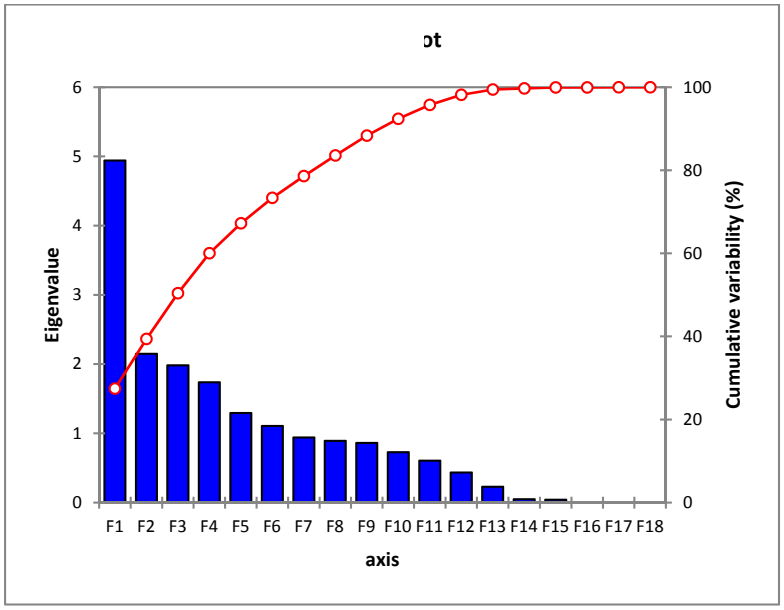

Figure 59. Scree Plot

Table 35 shows the eigenvalues/ factors for the data represented in the Scree plot. Nothing is particularly significant in any factor other than factor 1, which includes all of the weather conditions.

Table 35. Eigenvectors/ Factors: Measure of the Relative Contribution of the Variable to the Factor

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
Eigenvalue	6.87	2.63	2.46	1.88	1.79	1.4	1.24	1.2	1.17	1.17	1.16
Variability (%)	20.83	7.99	7.47	5.71	5.43	4.25	3.77	3.63	3.56	3.54	3.53
Cumulative %	20.83	28.83	36.3	42	47.45	51.71	55.48	59.12	62.68	66.23	69.77

Table 36 shows the eigenvectors for the first 11 Factors– Factor 1 is all related to weather issues but none are strong contributors. In fact, across all 11 factors there is no significant (>0.7) contribution by any one or group of variables to a factor, which suggests the variable of interest – odor complaints, is random.

Table 36. Eigenvectors representing the first 11 factors

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
No of complaints	0.035	-0.145	-0.044	0.606	-0.27	-0.011	0.035	-0.031	-0.026	0.018	0.011
No of Comp (0 or 1)	0.038	-0.142	-0.036	0.6	-0.28	0.003	0.057	-0.023	-0.027	0.031	0.005
compl t-1	0.033	-0.11	-0.022	0.124	-0.06	-0.062	-0.242	0.281	0.102	0.006	0.011
compl t-2	0.017	-0.089	0.031	0.09	-0.04	-0.199	-0.396	0.146	-0.128	-0.024	-0.005
compl t-3	0.004	-0.049	0.063	0.066	0.001	-0.275	-0.295	-0.075	0.088	-0.096	-0.017
Sat	0.001	-0.018	0.016	-0.046	0.063	0.002	-0.112	0.147	-0.051	0.524	0.615
Sun	-0.004	0.022	0.028	-0.081	0.077	-0.124	-0.09	-0.12	-0.058	-0.219	-0.018
Mon	-0.003	0.03	0.018	0.041	-0.01	-0.077	0.337	-0.48	-0.26	0.333	-0.363
Tue	0	0.013	-0.018	0.077	-0.07	0.044	0.476	0.172	0.195	-0.308	0.399
Wed	0.001	-0.004	-0.027	-0.012	-0.03	0.132	-0.069	0.623	-0.148	0.229	-0.493
Th	0.002	-0.026	-0.01	0.009	-0.03	0.07	-0.347	-0.182	-0.459	-0.495	0.091
Fr	0.003	-0.017	-0.006	0.013	-0.01	-0.048	-0.196	-0.159	0.781	-0.063	-0.23
Rain t-1	0.076	-0.064	-0.206	0.005	0.136	-0.093	-0.066	-0.063	0	0.138	0.037
Rain t-2	0.053	-0.034	-0.115	0.026	0.048	-0.078	-0.221	-0.226	0.005	0.243	0.121
Rain t-3	0.042	-0.018	-0.063	0.037	0.019	-0.087	-0.195	-0.237	0.066	0.257	0.072
Temp t-1	0.332	0.156	0.13	0.003	-0.04	0.024	-0.017	0.031	-0.007	0	0.009
Temp t-2	0.31	0.175	0.146	-0.015	-0.04	-0.051	-0.043	0.016	-0.02	-0.003	-0.002
Temp t-3	0.287	0.186	0.147	-0.013	-0.04	-0.05	-0.047	-0.018	-0.009	0.017	0.005
ow wind -1	-0.141	0.378	-0.279	0.088	-0	0.032	-0.046	0.001	-0.003	0.006	0.016
low wind -2	-0.133	0.258	-0.289	0.086	0.016	0.412	-0.133	-0.06	0.034	0.002	0.021
low wind -3	-0.114	0.136	-0.248	0.059	0.019	0.498	-0.163	-0.088	0.038	0.011	-0.011
Temp High	0.327	0.159	0.149	0.034	-0.04	0.106	-0.011	-0.013	0.025	0.01	0.006
Temp Avg	0.324	0.244	0.121	0.085	0.032	0.087	-0.015	-0.005	0.017	0.003	0.004
Temp Low	0.301	0.291	0.094	0.115	0.084	0.068	-0.017	0.001	0.011	-0.003	0.001
Hum High	0.177	-0.389	-0.126	-0.022	0.236	0.115	0.018	-0.004	-0.002	-0.024	-0.014
Hum Avg	0.229	-0.217	-0.166	0.122	0.436	0.092	0.037	0.016	-0.006	-0.049	-0.026
Hum Low	0.198	0.006	-0.146	0.209	0.467	0.043	0.038	0.026	-0.006	-0.051	-0.029
P High	-0.278	0.098	0.266	0.187	0.287	-0.057	-0.012	0.026	-0.002	0.011	-0.002
P Avg	-0.256	0.115	0.316	0.204	0.301	-0.021	-0.016	0.019	0	0.012	0
P Low	-0.235	0.127	0.343	0.207	0.307	0.011	-0.02	0.01	0.006	0.014	0.001
Wind Speed Avg	0.019	0.216	-0.339	0.051	0.038	-0.452	0.083	0.119	-0.03	-0.028	-0.016
Wind Speed Low	-0.121	0.393	-0.247	0.051	-0	-0.29	0.011	0.069	-0.028	-0.031	0.001
Precip	0.091	-0.048	-0.268	0.044	0.248	-0.216	0.124	0.058	-0.021	-0.082	-0.031

The factor loadings in Table 37 are used to determine relative weight. For example, the temperature and humidity may be large numbers, while precipitation is small. The factor loadings indicate if a given variable or group of variables is significant to the explanation of variance. Here, F1 (temperature and pressure) were the major contributors, albeit negatively to another (high pressure and low temperature and vice versa). Warm, high humidity and low pressure days are suggested as potential explanations for explaining complaints. No other factor had weights above 0.7.

Table 37. Factor Loadings Representing the Weights for Each Input Parameter

	F1	F2	F3	F4	F5	F6	F7
No of complaints	-0.107	-0.065	-0.079	-0.026	0.388	0.437	-0.584
days -1	-0.106	-0.138	-0.043	-0.03	0.489	0.339	-0.158
Days -2	-0.019	-0.124	-0.009	0.011	0.631	-0.04	0.088
Days -3	0.022	-0.042	-0.056	0.014	0.512	0.147	0.707
Temp High	**-0.759***	0.517	-0.158	-0.204	0.005	0.07	0.05
Temp Chg	-0.077	0.237	-0.308	-0.24	-0.311	0.643	0.159
Temp Avg	**-0.748***	0.629	-0.131	-0.045	0.048	-0.021	0.014
Temp Low	**-0.693***	0.671	-0.101	0.073	0.077	-0.089	-0.013
Hum High	**-0.591***	-0.598	-0.342	0.072	-0.046	-0.014	0.065
Hum Chg	-0.296	-0.383	-0.351	0.088	-0.338	0.394	0.135
Hum Avg	-0.723	-0.291	-0.378	0.412	0.019	-0.13	-0.02
Hum Low	-0.597	0.074	-0.285	0.574	0.071	-0.188	-0.088
P High	**0.812***	0.163	-0.429	0.305	0.029	0.013	-0.013
P Avg	**0.773***	0.238	-0.504	0.274	0.031	0	-0.015
P Low	**0.725***	0.29	-0.55	0.24	0.023	-0.008	-0.01
Wind Speed Avg	-0.097	0.094	0.559	0.602	-0.048	0.323	0.064
Wind Speed Low	0.29	0.345	0.539	0.494	-0.038	0.183	0.045
Precip	-0.322	-0.223	0.122	0.534	-0.107	0.065	0.02

***Group of variables significant for explaining variance of odor complaints**

A Varimax graph (Figure 60) is useful to visualize the relationships between variables. Here temperatures were correlated, humidity was correlated, and pressure was correlated, but they were not correlated with each other (within 45 degrees on one another). Low wind and pressure had some relationship. Odor complaints did not correlate to any of these variable (it is at the central axis). Hence the complaints appear to be random, and not related to weather.

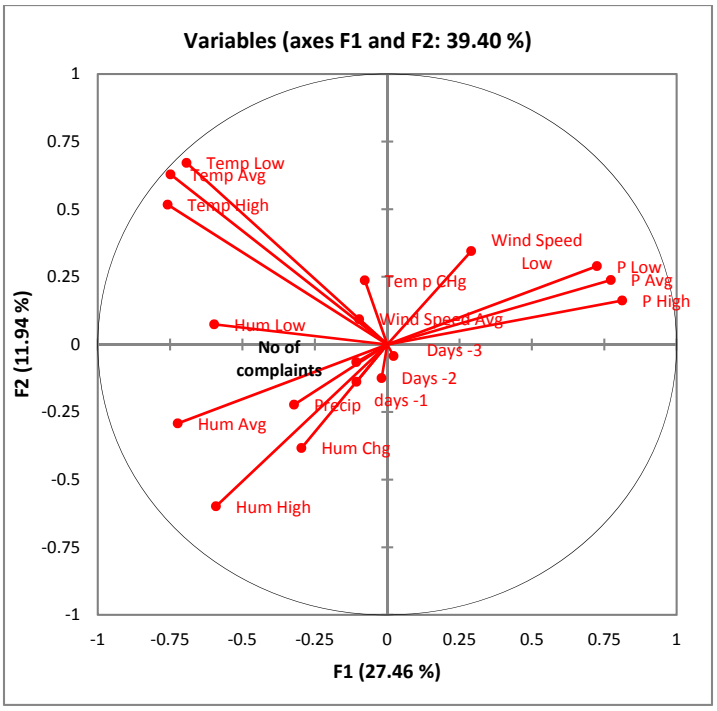

Figure 60. Varimax Graph Illustrating the Relationship between the Variables

Table 38 shows the coefficients obtained for a regression model to predict complaints, but it is not very useful in highlighting the major issues.

Table 38. Standardized Coefficients used in Regression Model

Source	Value	Standard error	t
Day -1	0.091	0.016	5.705
Days -2	0.069	0.016	4.319
Days -3	0.037	0.016	2.296
Temp High	-0.228	0.186	-1.226
Tem p Chg	0.077	0.019	4.111
Temp Avg	0.421	0.406	1.035
Temp Low	-0.229	0.246	-0.931
Hum High	0.002	0.101	0.016
Hum Chg	-0.004	0.019	-0.217
Hum Avg	-0.079	0.172	-0.458
Hum Low	0.132	0.113	1.165
P High	-0.176	0.108	-1.63
P Avg	0.542	0.195	2.783
P Low	-0.418	0.119	-3.518
Wind Speed Avg	0.062	0.022	2.767
Wind Speed Low	-0.135	0.026	-5.225
Precip	-0.019	0.018	-1.041

Figure 61 shows the coefficients compared to one another. The largest coefficients are for temperature, wind speed, pressure and humidity (note they are also higher values) so this may or may not be meaningful.

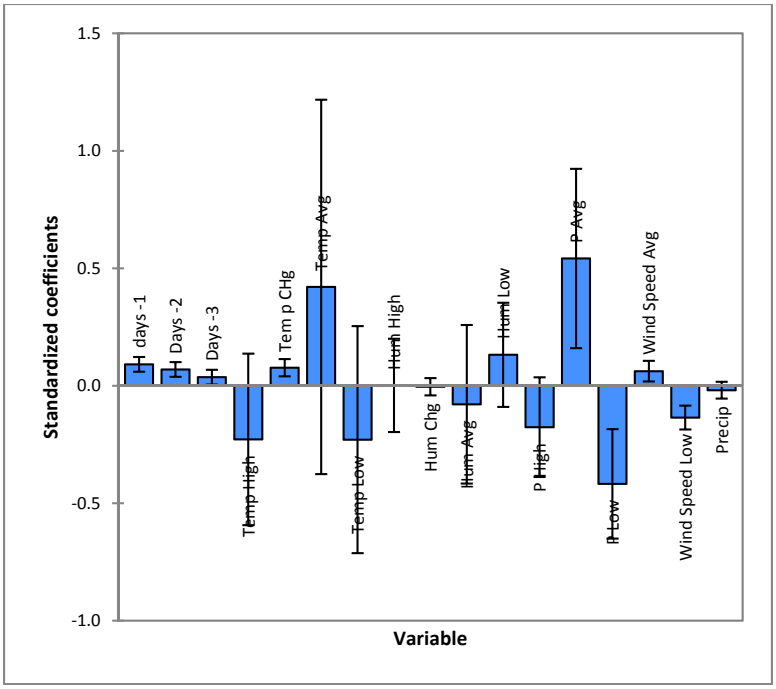

Figure 61. Standardized Linear Regression Coefficients at the 95% Confidence Interval

3.7 BACTERIAL EXPRESSION RESULTS

3.7.1 Results of Method 1 of Bacterial Expression of hOBPIIa

No transformants grew on the Kanamycin-LB-Agar plates incubated using Method 1 protocol of bacterial expression. Since there were no transformants, the protein could not be synthesized.

3.7.2 Results of Method 2 of Bacterial Expression of hOBPIIa

Healthy transformants grew during bacterial expression of hOBPIIa Method 2. The Bradford Assay performed on the samples after induction are presented in Table 39 and Figure 62. The sample with the lowest concentration of protein differed from the highest be a factor of ~4.

Table 39. Prior to protein purification, (A) optical densities of bovine serum albumin (BSA) standards and (B) protein concentrations (µg/µL) of cell extracts determined by dividing the measured optical densities by the slope of the standard curve

A. Bovine Serum Albumin (BSA) Standards				
Standard (µg)	**µL BSA stock (2 mg/mL)**	**µL water**	**µL 5X Bradford**	**$OD_{595\ nm}$**
0	0	800	200	0.000
2	1	799	200	0.151
4	2	798	200	0.363
6	3	797	200	0.574
8	4	796	200	0.711
10	5	795	200	0.848
12	6	794	200	0.941

B. Unknown Protein Concentrations of Cell Extract using 2 µL sample, 798 µL deionized water and 200 µL 5X Bradford Reagent			
Sample ID	**$OD_{595\ nm}$**	**Protein per sample vol. (µg)**	**Protein conc. (µg/µL)**
# 3 (induced)	0.286	3.22	1.61
# 7c (uninduced)	0.496	5.80	2.90
# 7 (induced)	0.750	8.91	4.46
# 2 (induced)	1.060	12.72	6.36

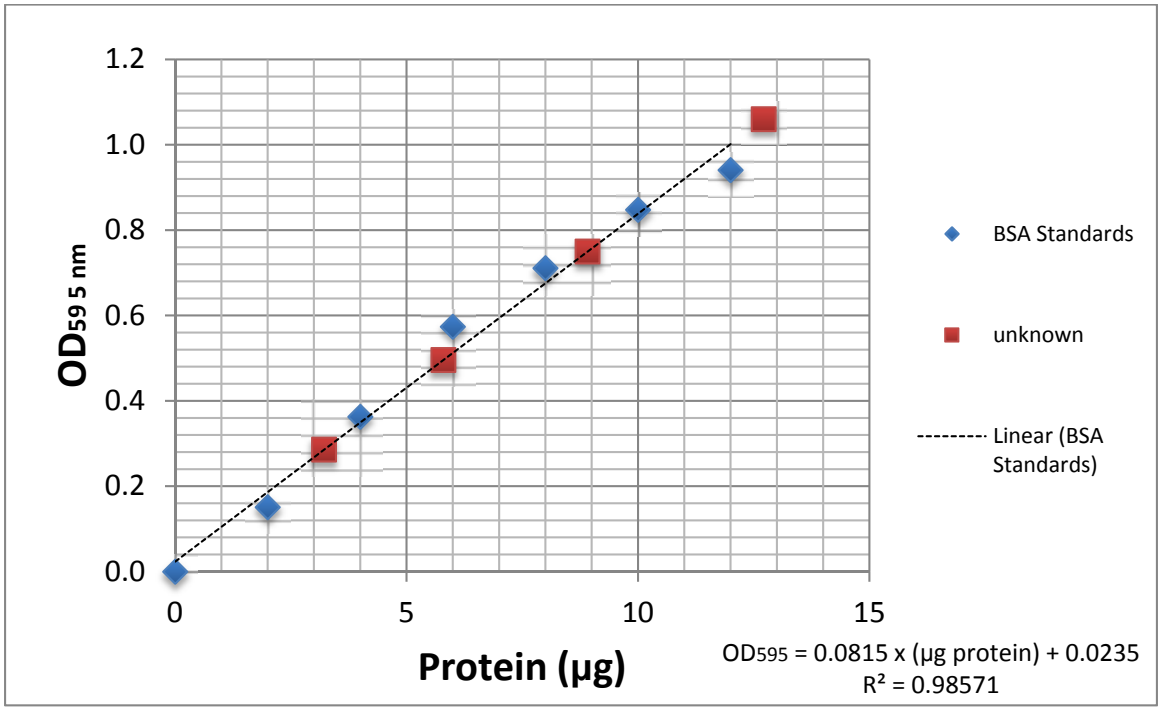

Figure 62. Plot of BSA standards and cell extracts of unknown protein concentrations

Following the Bradford Assay, the SDS-PAGE wells were loaded with the products of sonication: pellet of induced (1, 7, 13), pellet of uninduced (4), supernatant of induced (2, 8, 12), supernatant of uninduced (5), combined pellet+supernatant of induced (3, 9, 11), and combined pellet+supernatant of uninduced (6), as shown in Figure 63. Column 10 is the Novex Blue Kaleidoscope ladder, which did photograph well, but that did not interfere with interpretation of results. Columns 11, 12 and 13 are part of a second gel. Electrophoresis shows a strong signal band around ~20kD for all induced samples. The system produces analytical quantities of protein of the expected size, and the protein remains soluble as evidenced by the strongest signal in the supernatant of the induced samples.

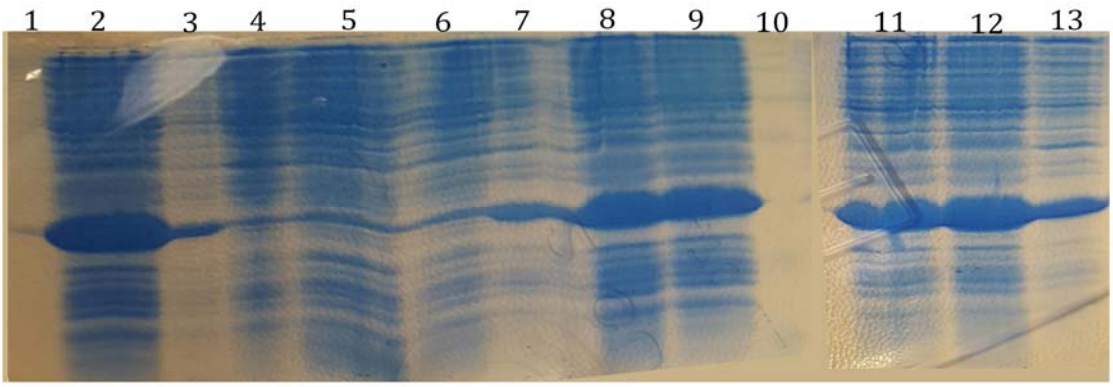

Figure 63. 12.5% SDS-PAGE electrophoresis of cell extract following sonication

After verifying through electrophoresis that the protein remained soluble, several rounds of protein purification were performed by chromatography using His SpinTrap TALON®, as summarized in Table 40.

Table 40. After protein purification trial 1, (A) Optical densities of BSA standards and (B) protein concentrations (µg/µL) of cell extracts determined by dividing the measured optical densities by the slope of the standard curve

A. Bovine Serum Albumin (BSA) Standards				
Standard (µg)	**µL BSA stock (2 mg/mL)**	**µL water**	**µL 5X Bradford**	**$OD_{595\ nm}$**
0	0	800	200	0
2	1	799	200	0.119
4	2	798	200	0.285
6	3	797	200	0.385
8	4	796	200	0.462
10	5	795	200	0.468
12	6	794	200	0.580

B. Unknown Protein Concentrations of Cell Extract using 2 µL sample, 798 µL deionized water and 200 µL 5X Bradford Reagent					
Sample Vol (µL)	**DI Water (µL)**	**5X Bradford Reagent (µL)**	**$OD_{595\ nm}$**	**Protein per sample vol. (µg)**	**Protein conc. (µg/µL)**
1	799	200	0.124	1.60	1.60
2	798	200	0.261	4.55	2.28
5	795	200	0.352	6.50	1.30

Following purification, a Bradford Assay (**Figure 64**) and verification (Figure 65) was performed, and SDS-PAGE electrophoresis was conducted again under the same conditions (Figure 66).

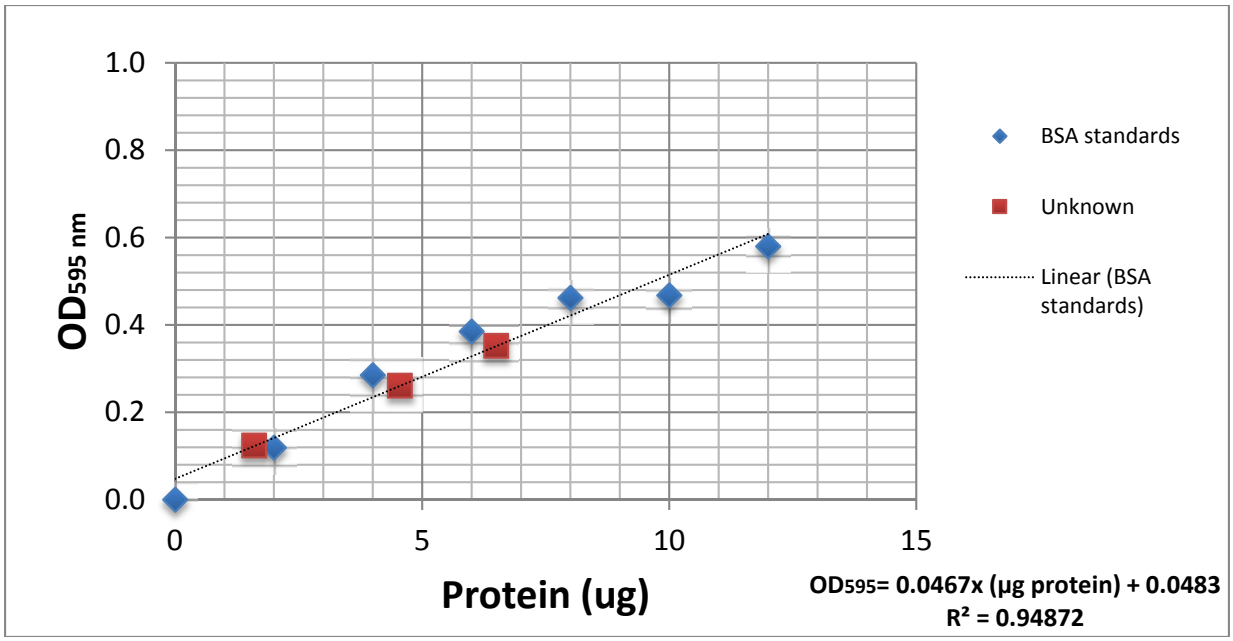

Figure 64. Plot of BSA standards and cell extracts of unknown protein concentrations before protein purification, trial 1

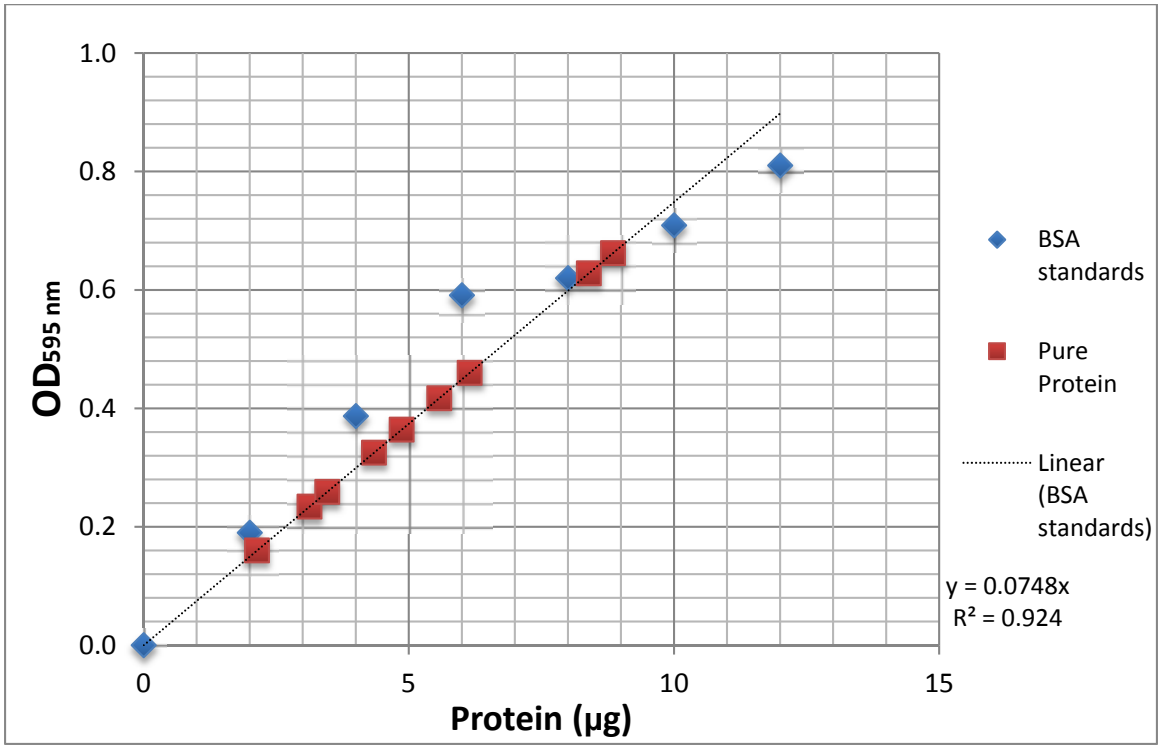

Figure 65. Plot of BSA standards and pure protein of unknown concentration after protein purification, trial 2

Optical density measurements for each sample of pure protein and subsequent protein concentration as determined using the slope of the Bradford standard curve are summarized in **Table 41**. The highest concentrations ranged from 1.23 – 1.77 µg/µL.

Table 41. Optical density measurements and protein concentrations for each sample of pure protein as determined using the slope of the Bradford standard curve; highlighted rows indicate which protein samples (2, 5, and 7) had the highest concentrations

Protein Sample ID	Sample Vol (µL)	DI Water (µL)	5X Bradford Reagent (µL)	$OD_{595\ nm}$	Protein per sample vol. (µg)	Protein conc. (µg/µL)
Pure Protein 1	5	795	200	0.234	3.13	0.63
Pure Protein 2	*5*	*795*	*200*	*0.628*	*8.40*	*1.68*
Pure Protein 3	5	795	200	0.364	4.87	0.97
Pure Protein 4	5	795	200	0.160	2.14	0.43
Pure Protein 5	*5*	*795*	*200*	*0.662*	*8.85*	*1.77*
Pure Protein 6	5	795	200	0.417	5.57	1.11
Pure Protein 7	*5*	*795*	*200*	*0.460*	*6.15*	*1.23*
Pure Protein 8	5	795	200	0.325	4.34	0.87
Pure Protein 9	5	795	200	0.259	3.46	0.69

Figure 66 compares electrophoresis results of various induced, unpurified supernatants after sonication (1, 3, 4, 6, 7) to uninduced, unpurified sample after sonication (2) to purified protein (5, 8). The strong band around 20 kDa is present in the induced, unpurified samples and not present in the uninduced sample, as expected. The same band is present in both of the purified protein samples with an estimated purity of approximately 95% as estimated by visual comparison with the example provided by the manufacture of the chromatography column, GE Life Sciences (Figure 67).

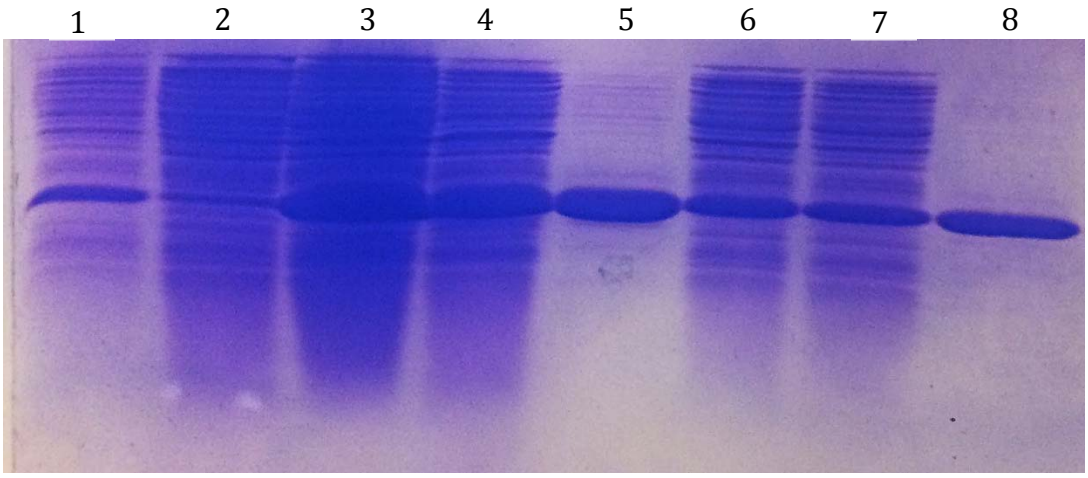

Figure 66. SDS-PAGE electrophoresis compares induced, unpurified supernatants after sonication (1, 3, 4, 6, 7) to uninduced, unpurified sample after sonication (2) to purified protein (5, 8)

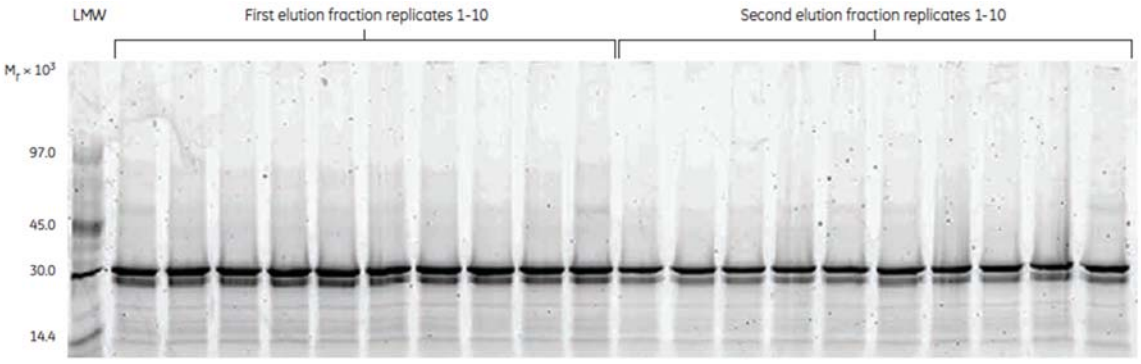

Figure 67. SDS-PAGE of elution fractions from ten replicate purification runs of GFP-His (Mr 28 000) using His SpinTrap TALON showing high purity (> 90%) of the eluted GFP-His (GE Life Sciences)

In an attempt to maximize the amount of protein produced, different IPTG concentrations and sonication times were varied, and the results are summarized in Table 42. The highest protein yields resulted from an IPTG concentration of 0.1 mM, the concentration recommended by the researchers who sent the original agar stabs (Ribeiro and co-workers). The highest yield of all trials was 3.23 µg/µL. The optimal sonication time was less clear. Since sonication is a relatively imprecise method, it is not possible to control for all variables. For example, depending on the angle and depth to which the operator places the probe in the sample, the intensity of the output power varies. Furthermore, the horn becomes fouled or pitted over time, and may also effect the distribution of sonication power to the sample matrix. Additionally, since the duration of each pulse, and the timing between each pulse delivered to the sample within the sonication period is not precisely measured and is manually controlled, it is not possible to know what effect those variations may have on the pure protein yield. However, since 6 minutes of sonication resulted in the highest yield (3.23 µg/µL) according to the Bradford assay (Table 42), this value was used for all subsequent protein purification steps. More experiments with precise control of the output intensity would be required to optimize the sonication time.

Table 42. Bradford Assays with differing induction and sonication parameters to determine optimal conditions that maximize protein yields

IPTG Conc (mM)	Induction Time (hours)	Sonication time (min)	sample volume (µL)	D.I. water (µL)	5X Bradford Reagent (µL)	OD_{595}	Protein per sample volume (µg)	Protein conc. (µg/µL)
0.1	6	4	2	798	200	0.43	6.35	3.18
0.1	6	5	2	798	200	0.263	3.88	1.94
0.1	6	6	2	798	200	0.438	6.47	3.23 - max
0.1	6	7	2	798	200	0.392	5.79	2.90
0.5	6	4	2	798	200	0.201	2.97	1.48
0.5	6	5	2	798	200	0.257	3.80	1.90
0.5	6	6	2	798	200	0.268	3.96	1.98
0.5	6	7	2	798	200	0.288	4.25	2.13

Bacterial expression of hOBPIIa using Method 2 was effective, and transformants were stored in glycerol at -80°C so the protein could be reproduced as long as the frozen stock is replenished any time it runs low. To replenish the frozen stock, some of the existing stock would need to be inoculated into fresh Luria broth and a new culture grown, mixed with glycerol and frozen in aliquots. Initially cells from each agar stab acquired from Portugal were kept separate throughout the expression and purification process since it was unclear if there might be any difference between them. Results did not indicate any significant differences in protein yield between the samples, so separation is no longer necessary.

A protein yield of 35 mg/L of culture was expected. Each of the pre-packed chromatography columns resulted in ~0.5 mL of protein in solution with an average of 1 mg pure protein/mL. Each column required 600 µL of post-sonication supernatant. Each liter of culture resulted in approximately 200 mL of cells. After sonication, suspension of cell extract in Buffer A, and centrifugation, approximately 20 mL of supernatant resulted. Thus each liter of culture could theoretically result in approximately 33 mg of protein, as predicted. However, producing large amounts of protein is limited by the small capacity of the pre-packed columns. For future protein production, larger capacity chromatography columns should be used, and fermentation should be scaled up. Such scale up to produce adequate volumes of protein would facilitate further parameterization and optimization of the biosensor. Additionally, care should be taken to ensure that the buffer in which the cells are suspended at any point before purification matches the buffer used in purification and the buffer used in the biosensor reaction, since buffer components can interact or may result in protein denaturation.

3.7.3 Binding Experiments

Figure 68 shows emission spectra during the first trial conducted in 50 mM K_3PO_4-KOH buffer at pH 7.5 with 1 µM hOBPIIa and 2 µM 1-AMA. Aliquots for 1 mL were extracted by pipette from the reaction chamber at 30, 50, 60, and 120 seconds, transferred to centrifuge tubes and measured using a spectrofluorometer in a 3 mL cuvette. The emission peaks for each aliquot are ~485 nm, which is expected for 1-AMA.

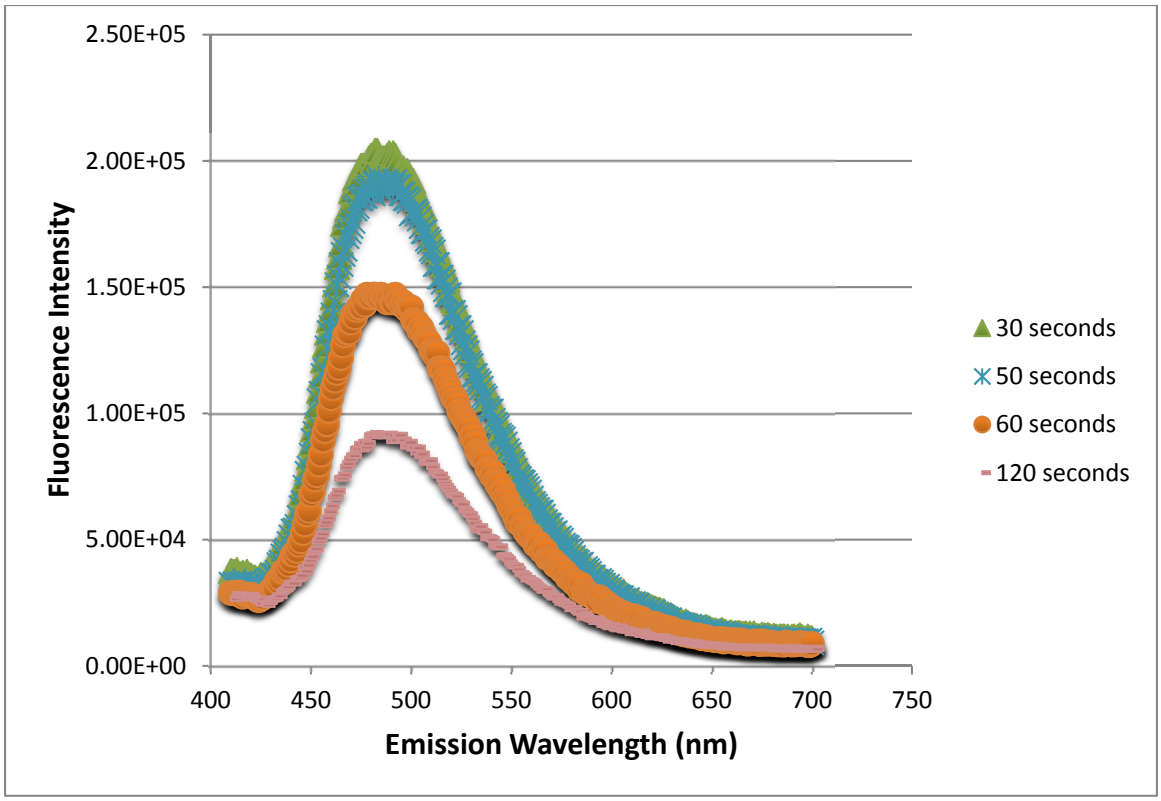

Figure 68. Spectrofluorometry emission spectra of hOBPIIa-1-AMA complex with increasing exposure to hydrogen sulfide

It is interesting to note that the peak fluorescence intensity appears to decrease in a linear fashion with increasing exposure time to hydrogen sulfide gas (Figure 69).

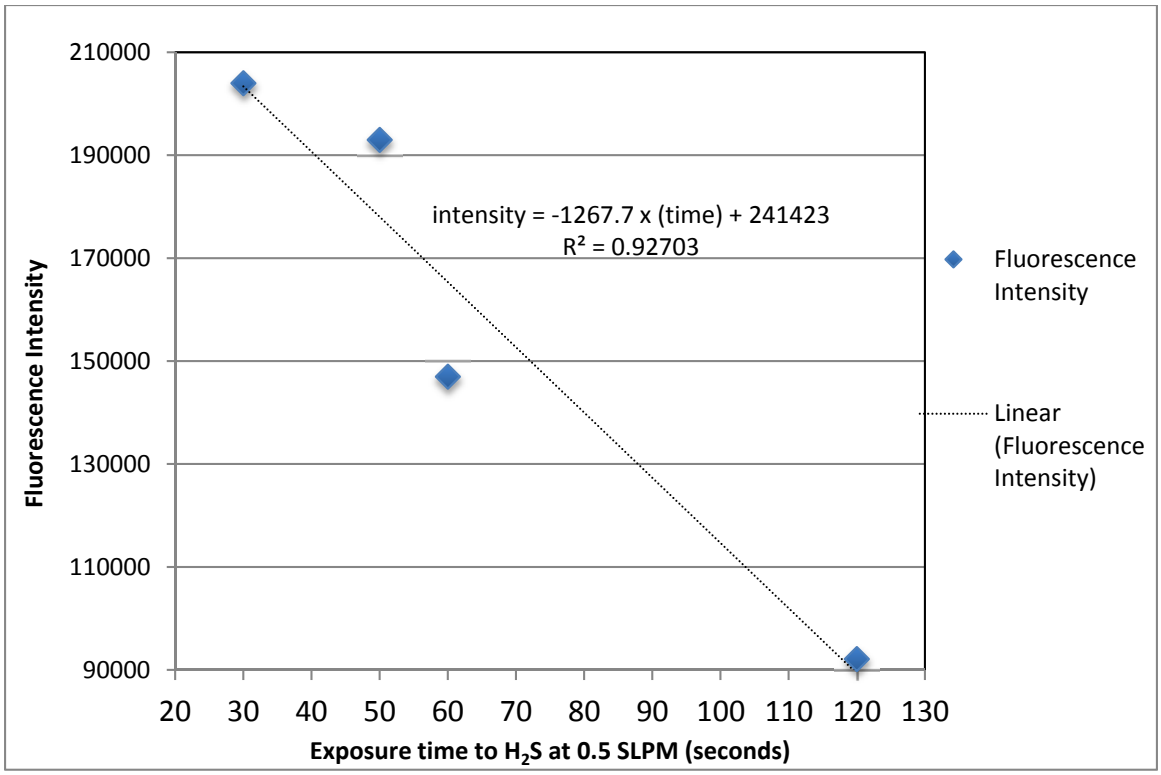

Figure 69. Plot indicating strong inverse linearity between emission peak intensity and hydrogen sulfide concentration

The reason that there are too few data points to be confident in the predictive power of the model in Figure 69 is that several of the data points were not included in the analysis because the plot of the spectral emission was particularly noisy at those points, potentially indicating that the light from the spectrofluorometer may not have been passing through the sample, but rather passing just above the sample, through the air. For these tests, a 3 mL quartz cuvette was used with 1 mL of each sample because sample volume availability was limited. By visual inspection, the sample volume inside the cuvette was high enough that the light should have passed through the sample, as appeared to be verified by the smooth emission spectra that resulted from several of the runs. The noisy emission spectra may have resulted from the cuvette being slightly tilted inside of the fluorometer (instrument was not level) or from a slight variation in the sample volume such that it was actually less than 1 mL for some of the samples. To avoid this type of error, future samples were loaded into a 1 mL quartz cuvette pictured in Figure 70.

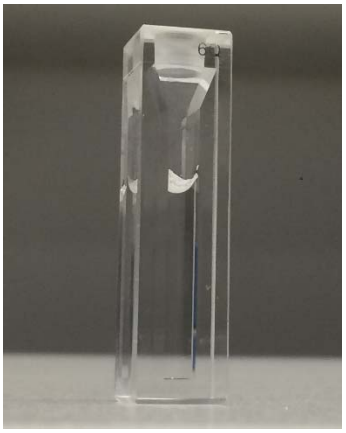

Figure 70. 1 mL capacity quartz cuvette containing 1 mL of sample

The maximum fluorescence intensity using the 3 mL cuvette was 2.1×10^5, which is significantly lower than the intensity of all the samples measured using the 1 mL cuvette (as high as 4.83×10^6). The reason for such magnitudes of difference (20x) can only be explained by the difference in cuvette geometry.

The linear model presented in **Figure 71** shows a strong inverse relationship between fluorescence intensity and the exposure time to hydrogen sulfide gas. The trendline crosses the x-axis at 190 seconds, which would indicate that binding saturation would occur for exposures beyond that time frame.

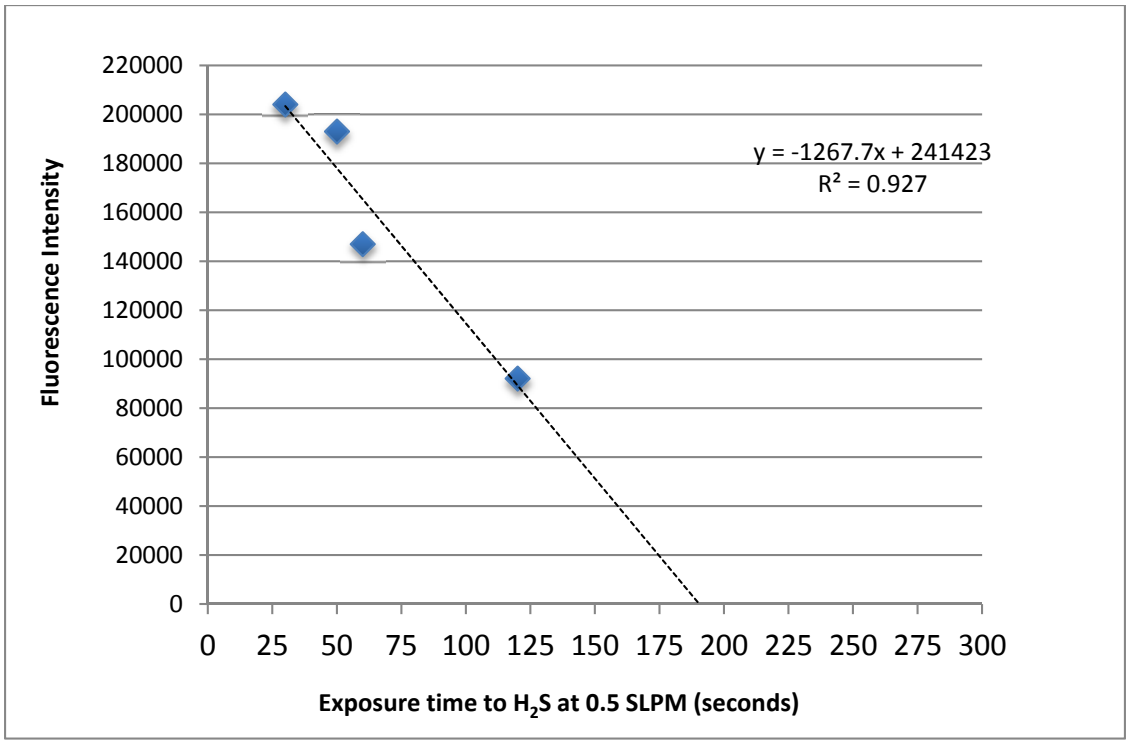

Figure 71. Plot indicating strong inverse linearity between peak fluorescence emission intensity and hydrogen sulfide exposure time

In the second round of testing, there was no observable change in the emission spectra at different H_2S exposure times. Since the fluorescence intensity increased so drastically in the second round from the first round of tests, the concentration of 1-AMA was lowered to 1 µM. At this concentration, the emission spectra again revealed a linear relationship with exposure to hydrogen sulfide gas. The fluorescence intensity was measured to be about 20 times higher than the first round of testing (when the 3 mL cuvette was used). Figure 72 demonstrates a decrease in the peak intensity with increased exposure to hydrogen sulfide, but to a lesser degree than in round one of testing and at an intensity orders of magnitude higher. The data point at 210 seconds does not follow the main trend and may be due to an error, which could be related to the binding saturation indicated previously at greater than 190 seconds of exposure.

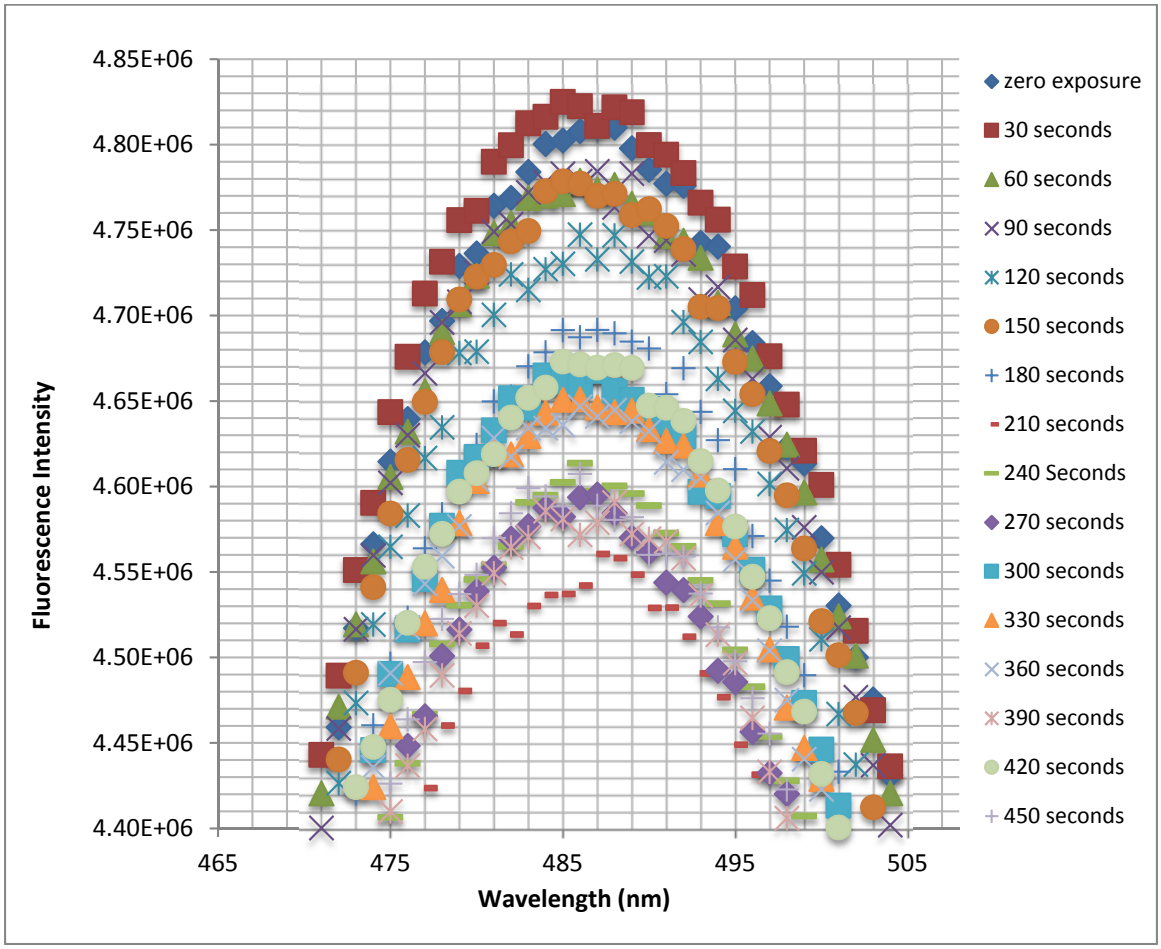

Figure 72. Plot of intensity of peak fluorescence emission at 380 nm excitation for round three of tests using a 1 mL cuvette

None of the components of the biosensor have measured fluorescence emission peaks at ~485 nm as the biosensor solution complex does. The biosensor solution complex is the only non-zero curve in **Figure 73** and is the only component that comes close in intensity and emission to those of the biosensor when exposed to hydrogen sulfide. However, the measured fluorescence intensity (7×10^6) is higher than any emissions when exposed to hydrogen sulfide ($4.5 – 4.8\times10^6$), indicating that the fluorescence of 1-AMA is enhanced when bound only to hOBPIIa.

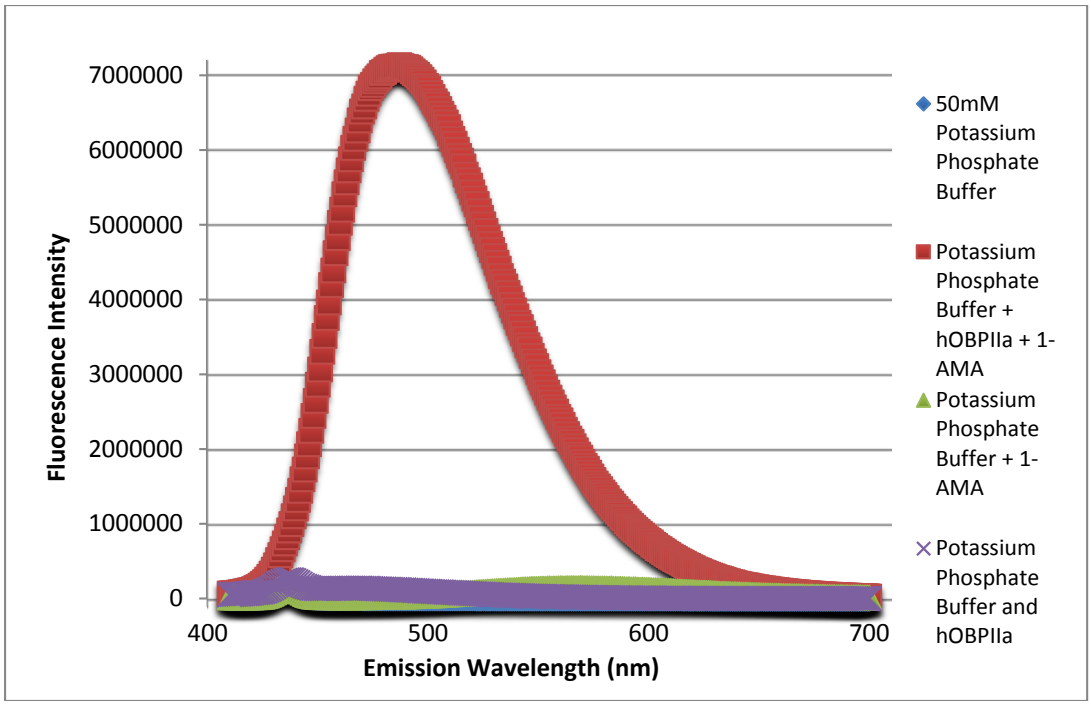

Figure 73. Plot of the florescence intensities in the band between 400 and 700 nm of all components of the biosensor solution when excited at 380 nm with 5nm slit widths for excitation and emission

In **Figure 74**, the biosensor solution complex was eliminated from the graph so that the scale could be reduced, and the data adequately visualized. The very narrow and pointy pseudo-peaks at between 400-450 nm are characteristic of light scattering and should not be considered peak emissions (Briand et al. 2000; Yvon 2014). Rather, the peak emissions are 461 nm for hOBPIIa alone in potassium phosphate buffer and 569 nm for 1-AMA alone in potassium phosphate buffer. All components are in identical concentrations as they were in the binding experiments.

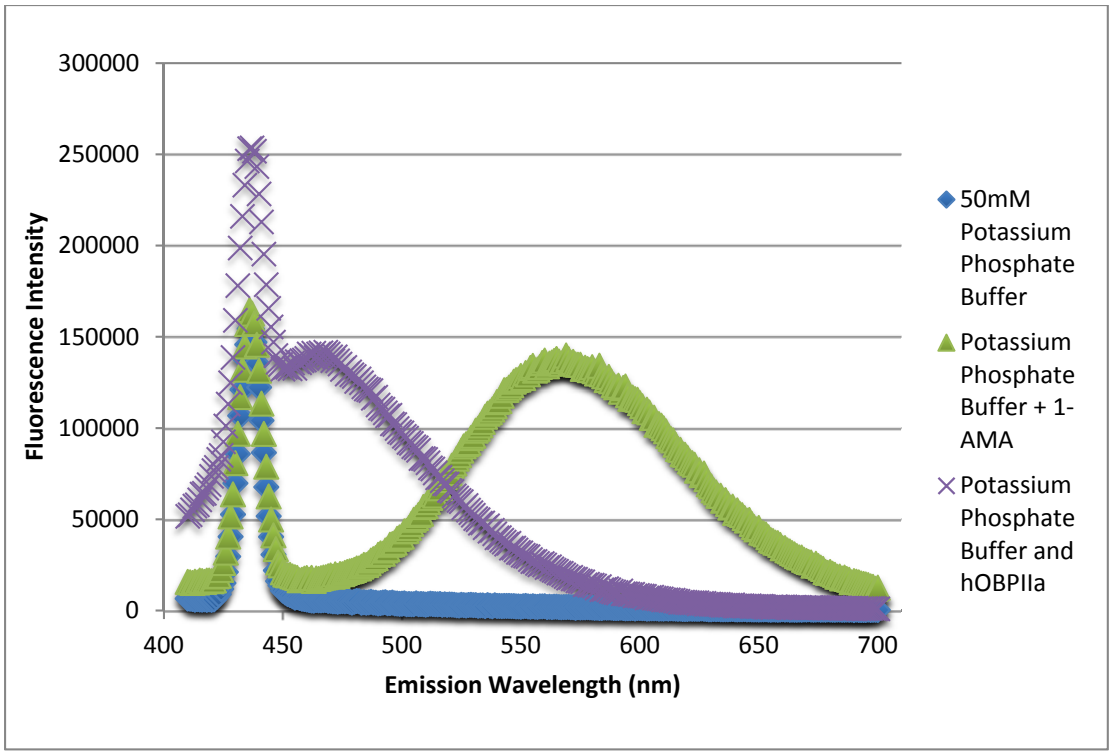

Figure 74. Plot of the florescence intensities of all components of the biosensor solution except for the potassium phosphate buffer+hOBPIIa+1-AMA complex

3.7.4 Linear Regression

As plotted in Figure 75 of the first round of testing, there was an inverse linear relationship between fluorescence intensity and the amount of time the hOBPIIa-1-AMA complex is exposed to hydrogen sulfide gas.

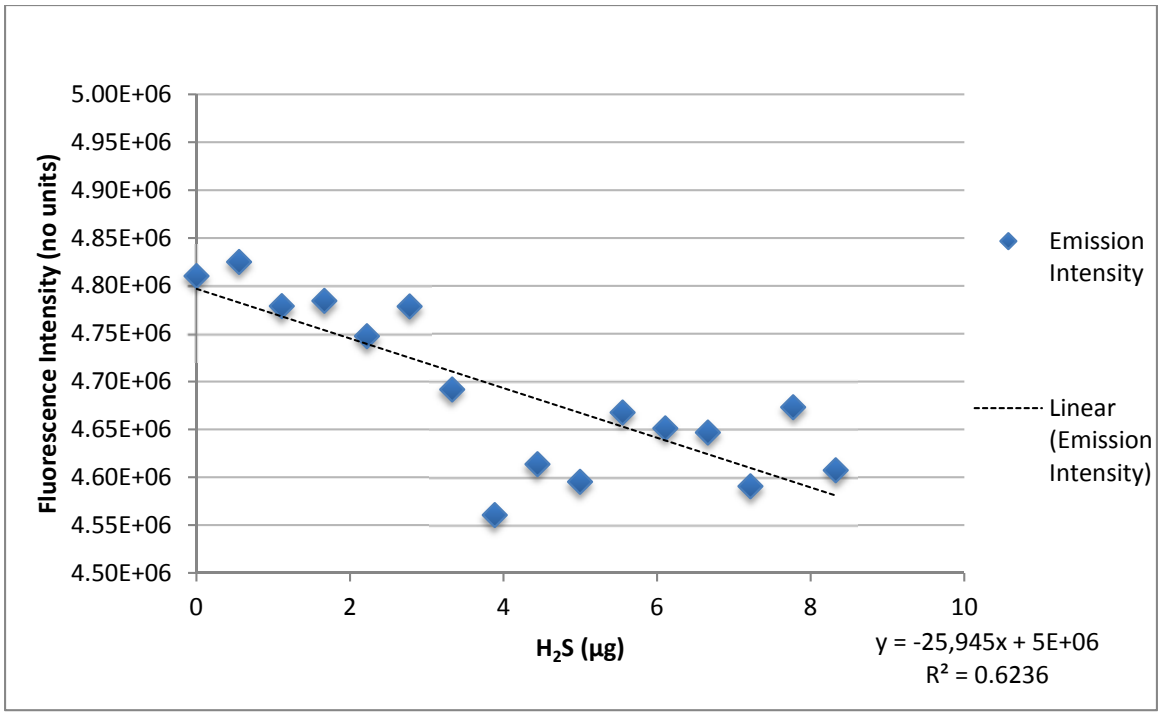

Figure 75. Linear regression from third data set showing a decrease in maximum fluorescence intensity with increasing hydrogen sulfide exposure

Visual inspection reveals that the relationship appears to have two portions of the curve: 1) the initial portion is linear up to 200 seconds and 2) the second portion appears to have a flat slope with more scatter, potentially suggesting the sensor proteins have reached saturation (refer to Figure 76).

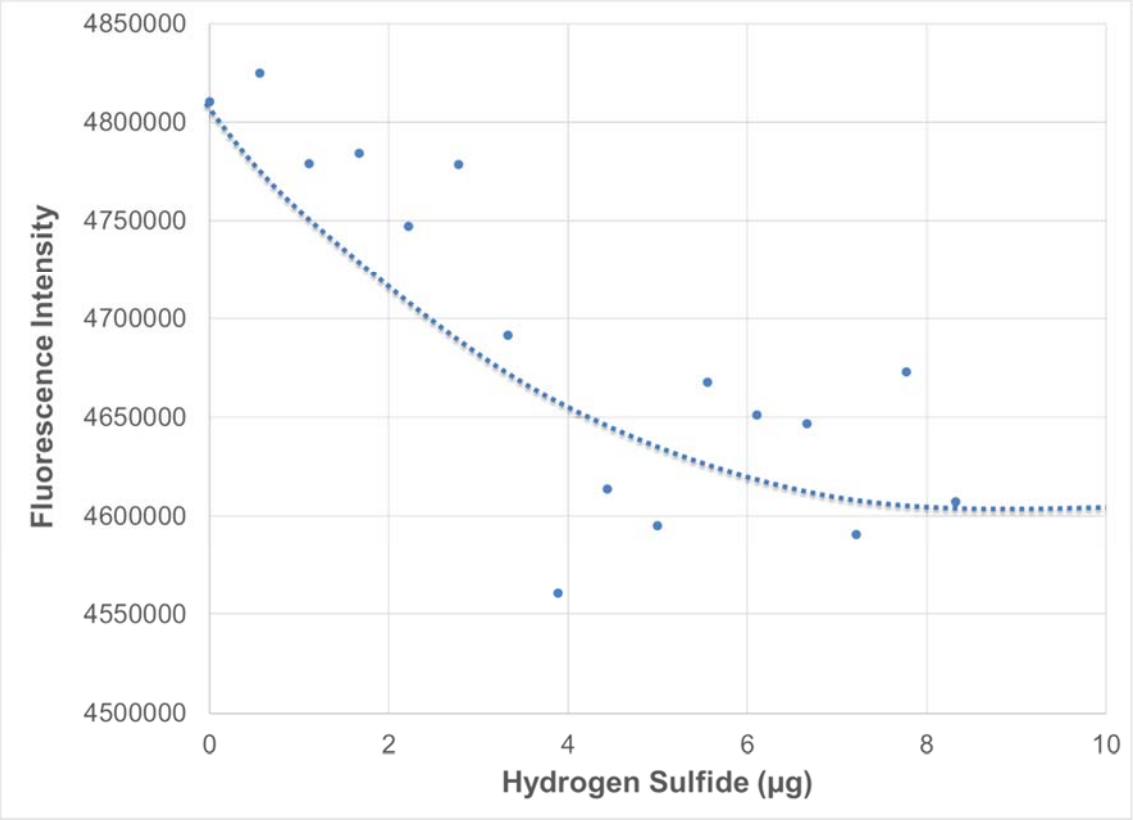

Figure 76. Linear regression from third data set showing a decrease in maximum fluorescence intensity with increasing hydrogen sulfide exposure until 4 µg with a slope of -52,626, then a saturation level asymptote is suggested, with a nearly flat slope of 2340.

To develop a predictive model that would allow fluorescence emission spectra from the biosensor to determine the amount of amount of unknown odorous gas present within a reasonable level of confidence, the hydrogen sulfide exposure was converted to µg H_2S using the flow rate. Scatter increases above 4 µg. Again the scatter may be caused by saturation of the proteins, giving an uncertain result. Future testing should include higher protein concentrations to verify linearity and saturation.

4. CONCLUSION

4.1 SUMMARY OF MAJOR FINDINGS

4.1.1 Meteorological Conditions

With all the issues that solid waste facilities are facing when nuisance odors are involved in consideration, management of facility must give attention to operating the facility in a manner that would reduce any potential impact to nearby neighborhoods. By monitoring meteorological conditions, assumptions can be made in order to predict possible situations when odor complaints could occur. With atmospheric conditions being so complex, it is difficult to exactly forecast what will happen in the future.

Databases on odor complaints were provided by two different landfill sites, both operating in close proximity to residential areas. Data in this study was used with the aim to investigate the existence of patterns or trends, if any, in the relationship between frequencies of odor complaints with the influence of meteorological parameters of interest: temperature, humidity, pressure, wind direction, wind speed, precipitation accumulation, weather conditions and events present at the time.

Preliminary analysis of the days when odor complaints occurred at Urban Site 1 showed the possibility for pattern identification since there was a presence of a trend that occurred in all the situations when odor complaints were received. In all scenarios, odor complaints were received while the wind speed was weak (<1 mph), wind direction was from the south, temperature and pressure decreased from the previous day and the absence of precipitation or rain events was noted. Also, the weather conditions were stable with mostly cloudy skies. The dry season, from November until April, showed higher frequency of odor complaints for Urban Site 1, while for Urban Site 2 it was the wet season (May until October). Slightly more odor complaints were made in the afternoon hours and during working days, probably because on the weekends people tend to spend their time outside the house and in the afternoon hours, since people are coming home from work and spending more time at home. Locating the odor complaints on the map revealed clusters of complaints and communities with the highest frequency of complaints, in a relationship with the predominant wind directions for that particular location. Correlations between meteorological parameters, both for Urban Site 1 and Urban Site 2, showed that wind direction and wind speed were the parameters with lowest correlations when compared to the values from the day before, which is expected since those are meteorological parameters with the lowest expected predictive ability, while temperature, humidity, and pressure had constantly higher correlation values. Also, a highly negative Pearson correlation coefficient ($r_1 = -0.73$; $r_2 = -0.94$) was identified between temperature and humidity, which results in increases in temperature if humidity decreases and vice versa.

Analysis of isolated odor complaints (three or more complaints in the same day) with meteorological parameters, for both sites, revealed there is an absence of correlations between them. An analysis was also performed based on dividing the data set into dry (November until April) and wet (May until October) season, which showed that higher frequency of odor complaints, in the case of both sites, tended to occur in the dry season. Results obtained for the dry season for the Urban Site 2 identified pressure drop as a parameter with the highest observed correlation with frequencies of odor complaints. Precipitation accumulation data analyzed for the day before, three days and seven days before showed no correlation with number of odor

complaints for Urban Site 1. However, for Urban Site 2, results showed that the number of complaints could be related to the amount of precipitation that has been accumulated three days prior the odor complaints, which could indicate a different type of odor source.

Since until this point in the analysis, strong correlation between meteorological conditions and frequency of odor complaints was not identified, additional dates with days when odor complaints did not occur have been added to the original complaint data set. Results obtained also showed no correlation between the frequency of odor complaints and meteorological conditions. When segregating the data set into dry and wet season, Urban Site 2 showed higher number of odor complaints in the wet season, which could be related to the influence of precipitation accumulation this site is experiencing. Meteorological parameters for both sites showed the same trend for dry and wet seasons, except the difference in higher number of complaints, which for Urban Site 1 occurred in dry season and for Urban Site 2 in the wet season. Also, it was noticed that more stable weather conditions tended to occur in dry season. Autocorrelation analysis of odor complaint frequencies indicated no potential in predicting the number of odor complaints from one day to the next.

Analysis of the isolated days (three or more complaints in the same day) and random days without complaints but with similar meteorological conditions was performed with the goal to potentially distinguish the weather patterns when complaints actually occurred compared to those when no complaints were filed. Results revealed that the pattern for weather conditions when odor complaints could potentially occur cannot be identified since there is a presence of the same trends in meteorological conditions, both when complaints actually occurred as well as when there was an absence of same. Wind directions in the case of Urban Site 1 were related to the odor complaints since most of the complaints were coming from the communities located south and SE from the landfill site. In the case of the Urban Site 2, a different pattern was observed. Both, on the day with or without complaints, the most frequent wind directions were very similar. Wind speeds prevailing in both locations were from 8-12 miles per hour. For weather conditions, both sites again showed different patterns. In the case of the Urban Site 1, odor complaints were related to mostly cloudy skies, while in the case of the Urban Site 2 clear skies were dominant. When analyzing the meteorological events occurring for each scenario, both sites had the same trend. The most frequent event identified, whether or not complaints were present, was the absence of rain. Also, it was noticed that on days with no odor complaints, rain was more frequent.

PCA suggested warm, humid and low pressure days as potential explanations for frequency of odor complaints. It showed relationships between heat, wind, humidity and pressure on a given day, and some relationships between those variables but none with the number of complaints on a given day, nor with weather patterns on prior days, which suggested that the odor complaints are random since no limited number of factors accounts for the majority of the variance. Linear regression showed that temperature, pressure, wind speed and humidity had the largest impact (note they were also higher values) on frequency of odor complaints, so this may or may not be meaningful. From the results obtained, it could be noticed that meteorological parameters alone do not have the ability to predict when odor complaints could potentially occur. The decision to file an odor complaint is affected by many other factors, not just with the presence of meteorological conditions. There could conceivably be a situation when odor was detected, and the person would immediately file a complaint to site personnel, and in a similar situation, it

could be that the person will procrastinate for some time or even days after first detecting the odor to make a complaint, and in a third possibility, the person may detect the odor but not bother to, or not know how to, file an official complaint, which makes it very difficult to verify and relate to the presence of complex weather conditions. Even though more odor complaints tend to occur when there is an absence of rain, information in this study revealed that rainfall accumulated from up to three days before could trigger odors and eventually a filing of a complaint. Different results from the two separate sites could indicate that odor complaints are occurring randomly and attempting to analyze only one scenario in which they could potentially occur might be an oversimplification of a complex phenomenon. Other reasons could be related to the variability of the data sets collected, the presence of outliers, more detailed data collection on odor complaints, etc.

After the detailed analysis of the data sets, some of the findings suggested empirical but not statistically significant relationships between complex meteorological conditions and frequency of odor complaints. Those found were similar to ones recognized in the literature review (Table 43). More odor complaints were noticed during weak winds and stable weather condition (mostly cloudy skies) because odors tend to linger longer with less mixing and less diffusion. When there was an absence of rainy events, odor complaints were more frequent since rain serves as a cleanser of the air. Dry season, from November to April, was identified with higher potential for odor annoyances. Possibly related to the lack of rain or residents spending more time outside, increasing potential exposure time. Pressure drop was also identified as a potentially interesting factor, since on the days when pressure values would decrease compared to the previous day, there was a tendency of finding more odor complaints filed.

Table 43. Summary of Findings from This Study Relevant to the Literature Review

Factor	Conditions	Impact	Reference	Findings (This Study)
Wind speed and direction	• Weak wind, stable conditions • Clear, strong wind, low variability in wind direction	• Highest odor detection • Significantly lower odor detection	(Capelli 2008)	More odor complaints noticed on days with weak winds (<1 mph or 8-12 mph most frequent)
Temperature	High	• Higher odor detection • Unstable conditions	(USEPA 2000)	Heat stimulates odor complaints

Factor	Conditions	Impact	Reference	Findings (This Study)
Precipitation	Low	• Wet soil prevents LFG migration • Rain seepage into the pore spaces pushes out gases into the atmosphere	(ATSDR 2017)	Absence of rainy days resulted in higher frequency of odor complaints
Humidity	High or foggy	• Higher odor detection • Warm humid air enhances human sense of smell • Traps smells so they linger longer	(Berglund 1998)	Higher humidity related to tendency of occurring odor annoyances
Weather conditions	• Clear sky, sunny and windy • Overcast, no wind, high humidity/fog, thermal inversions	• Complaints rarely received • Complaints are more common	(MassDEP 2007)	Cloudy skies revealed higher potential for odor annoyance
Thermal inversions	Season changes (Fall → Winter, Winter→Spring)	During the period of the year in which inversions are more common, odors are held more closely to the ground and are more likely to be detected	(NSWMA 2008; Energy and Environmental Affairs 2016)	Dry season (November-April) revealed higher frequency of odor annoyances

Factor	Conditions	Impact	Reference	Findings (This Study)
Pressure	Low	More LFG seeps into the air	(USEPA 2000)	Pressure drop revealed higher tendency of occurring odor complaints

4.1.2 Biosensor Development

One major contribution of the development of the biosensor work has been establishing effective protocols for successfully cloning and inducing the supplied *E.coli* transformants and purifying hOBPIIa from them. The protein was determined to remain soluble, and cobalt-based immobilized metal affinity chromatography columns resulted in ~95% pure hOBPIIa. Inducing with 0.1 mM IPTG with 6 minutes of sonication resulted in the highest protein yield (3.23 μg/μL). Repeated trials revealed that each liter of culture could result in approximately 33 mg of protein. For the first time, hOBPIIa complexed with 1-AMA has been used to detect hydrogen sulfide concentrations by spectrofluorometry. The ratio of hOPBIIa:1-AMA was determined to be approximately 1:1. From the data collected, a promising linear regression model was generated that could be used to predict hydrogen sulfide concentrations from peak fluorescent emission intensity measurements within a range of 0-8.3 μg of hydrogen sulfide. A novel experimental exposure chamber prototype was developed that has the potential to be incorporated into a portable sensor because it is relatively compact.

4.2 RECOMMENDATIONS

Since the human sense of smell is highly subjective (Philpott et al. 2006), an effective procedure to investigate and manage odor issues must be developed. Odor complaints can help site personnel to identify conditions and events that potentially lead to a nuisance odor complaint. Considering that residents living close to the landfill site can be present 100% of the year, they can provide valuable input. Once awareness about specific activity that could trigger an odor event is recognized, site managers can investigate the source and implement suitable actions. Any site activity prone to producing odors should take into consideration complex weather conditions, especially wind direction and wind speed, since those are parameters responsible for physically dispersing odors off-site. Installation of a weather station at the site and collecting relevant meteorological data can help to identify if the site could be responsible for causing the odor event. Keeping an extensive internal odor report log at all times, making a note of all site activities that could lead to producing odors, would be a valuable tool to be used when investigating the sources of odor complaints.

With the aim of better identifying the relationship between the odor complaints and meteorological conditions, it is necessary to obtain data about the solid waste operations at the site. One of the limitations of this study was inconsistent information about the time that the odor

was first noticed (not just the time of a complaint), so it can be related to meteorological condition and site activities. Another major limitation was an absence of comprehensive site records about waste operations, limiting the possibility to track historical records. With that being said, there is a need to substantially improve the amount of valuable information provided in odor complaint logs as well as in the site records. Implementing an effective site diary to keep track of the activities present at the site would be a valuable asset for dealing with odor episodes. In order to successfully identify the source of odor, perceived by the people living and working close to the landfill site, data on solid waste operations should be recorded so that it could be mined. Insufficiency of both, suitably exhaustive site and complaints documentation, prevented better interpretations of the data collected in this study.

Odor complaints and data on solid waste operations should be compared using a detailed analysis of meteorological conditions and operations cross-compared to the actual time of the odor episode not the time the complaint was filed. In addition, further investigation of the influence of pressure drop and atmospheric stability class on odor complaints should be performed because these parameters are not routinely recorded in most typical weather stations. Atmospheric stability class for each day could be identified through temperature gradient or temperature lapse rate method. This method uses the vertical temperature gradient ($\Delta T/\Delta z$) between two levels: in this case, at the top of the hill (landfill body) and at the ground level (fence line). By knowing those values, calculated temperature gradients can be compared to Table 44 with Pasquill Stability classes (A-F) to identify the stability class of that particular day.

Table 44. Pasquill Atmospheric Stability Classes

Pasquill Classes		**Temperature Gradient ($\Delta T/\Delta z$) (°C/100m)**
A	Extremely unstable	**($\Delta T/\Delta z$) <-1.9**
B	Moderately unstable	**-1.9≤($\Delta T/\Delta z$) <-1.7**
C	Slightly unstable	**-1.7≤($\Delta T/\Delta z$) <-1.5**
D	Neutral	**-1.5≤($\Delta T/\Delta z$) <-0.5**
E	Slightly stable	**-0.5≤($\Delta T/\Delta z$) <1.5**
F	Moderately stable	**1.5≤($\Delta T/\Delta z$) <4**

An example of this calculation is presented as follows:

T_1 = 10ºC T_2 = 2ºC

z_1 = 3000 m

z_2 = 5000m

Temperature gradient = ($\Delta T/\Delta z$);

Temperature gradient = (10-2) / (3000-5000)

Temperature gradient = -0.4ºC/100m

Then by the looking in the table, we can see that gradient of -0.4ºC/100m falls under category "E" or "Slightly Stable" for atmospheric stability class.

Installation of temperature and pressure sensors at the top of the hill and at the fence line would be the first step in collecting this potentially useful information. Finally, the strength of statistical correlations will always be dependent upon the size of the data set. If more urban landfill sites would participate by providing the necessary data, it would allow for more powerful analyses.

Further recommendations include revising the odor complaint verification form to obtain data that could lead to making strategic operational adjustments, developing a preemptive odor threat assessment level index, and performing an alternative analysis to identifying the most preferred odor management options available. Some of these suggestions are developed further as follows.

4.2.1 Revised Odor Complaint Verification Form

Since the human sense of smell is highly subjective (Philpott et al. 2006), an effective procedure to odor investigation must be developed. In an effort to gain more useful information from odor complaint logs with the aim of identifying patterns that could lead to the detection of nuisance odors in the community, the following recommendations should be considered. The main limitation of this study was that the databases that were provided only contained limited or inconsistent information on the environmental and operational conditions present at the site when the odor was actually detected offsite. Consistent odor complaint databases with relevant information at the exact time of the event would improve the understanding of why an odor complaint was filed. Background information is key to identifying the source of the odor and its frequency, duration and strength, when the odor was first observed as well as the most common descriptors about the odor that people detected. The following information is recommended to be included in the odor complaint verification form:

- Identifying if the person who made the complaint is a repeat reporter who calls often to complain because of hypersensitivity or because a real odor problem exists.
- Information on odor characteristics described by people who made a complaint could be used to help identify what are the most common odor descriptors and compare it to the days with highest number of complaints in the same day.
- Documenting time of an odor event when it was actually noticed, and not when the complaint is filed.
- Impact of weather data collected on parameters of interest: temperature, humidity, pressure drop, rain, wind speed, wind direction, etc. at the time of detected odor.
- Weather at the time of an odor event (Calm, fog, windy, rain, combination of weather conditions, additional).
- Asses the frequency of odor annoyances (Single incident or daily).
- Asses the intensity of odor (Likert scale: very light to very strong).
- Determine total duration of the odor (Example: 1 minute to 24 hours).
- Asses the frequency of odor complaints in respect with site operational activities known to produce odors (delivery and handling the waste, delays in covering an odorous waste, etc.)
- Asses the frequency of whether people would/do complain to distinguish if sufficient management practices have been employed or people normally do not complain (Odor events could be rare or poor strength).

- Determine if odor events are related to seasonal variations by differentiating between the diverse components (weather, time of the year, etc.), which could lead to odors (Dry season: November until April, Wet season: May until October)

All of this information would be valuable in resolving the source and transport pathway of the odorant. Proposed odor complaint log is presented in Figure 77**Error! Reference source not found.**. The proposed form is intended to be filled out by landfill personnel during a verification visit interview with the resident who filed the complaint.

ODOR COMPLAINT LOG FORM FOR LANDFILL ODORS

General Information

Date of Odor Complaint:

Name of the Person:

Address of Odor Complaint:

Time of Odor Complaint:

Time AM/PM:

Day in a Week:

Landfill in Proximity to Odor Observation:

Possible Source of Odor (Check the box that applies):

Waste receiving and processing ☐ Drilling Gas Wells Cover ☐

Scraping Daily or Intermediate Cover ☐ Digging Trenches ☐

"Other" _____

Description of Odor

What Time was Odor First Detected?

What Time was Odor Last Detected?

Duration of Odor (minutes or hours):

Location: Indoors/Outdoors:

Strength (1-5, with 1 being very light and 5 being very strong):

Character (Type):

Meteorological Conditions at Time of Odor Observation

Temperature (◦F): Wind speed (MPH):

Wind Direction: Sky Conditions:

Precipitation Accumulation (In): Pressure (In):

Humidity (%):

VERIFIED: YES / NO **Signature:**

Figure 77. Recommended Odor Complaint Log

4.2.2 Operational Adjustments

If odor complaints received have a trend of describing the same odor, it could potentially indicate that people are perceiving a common problem, suggesting a more appropriate action to be taken by the landfill manager. For example, by knowing which solid waste operations were involved, the best management and operational practices will be applied to minimize odor issues. Typical solid waste management operations that should be included in this adjustment are:

- Biosolids disposal
- LFG well drilling
- Excavating trenches
- Insufficient vacuum on the landfill to extract gas
- Adequate cover- daily or intermediate cover type and thickness
- Leachate seeps
- Collector clogging
- Waste receiving and processing activities
- Overly odorous loads
- Maintenance activities involving the tipping floor
- Unscheduled delays of routine activity at the active face due to breakdowns of equipment or personnel taking breaks

4.2.3 Odor Threat Assessment

In this study, the researchers were unable to develop a way to predict when an odor event will occur from individual meteorological parameters alone; however, certain key parameters have been noted in the literature and have demonstrated empirical relationships in this study, leading to the development of a proposed "Odor Threat Assessment Index". Assessment of potential key weather conditions for occurrence of odor complaints could assist landfill site personnel in deciding whether or not to alter daily operations on a particular day. Meteorological parameters considered are:

- Wind speed/wind direction
- Temperature/Humidity
- Precipitation
- Atmospheric Stability Class (A-F; with A=being extremely unstable and F=moderately stable)
- Pressure drop over the previous 24 hours

The threat level is divided into five different categories, representing the level of possibility of an odor complaint. Those five categories are as follows (Figure 78):

1. Critical: Odor complaints are expected immediately (Red color)
2. Severe: Odor complaints are highly likely (Orange color)
3. Substantial: Odor complaints are a strong possibility (Yellow color)
4. Moderate: Odor complaints are possible, but not likely (Green color)
5. Low: Odor complaints are unlikely (Blue color)

Figure 78. Odor Threat Assessment Levels based on the Possibility of an Odor Event

No wind or weak wind speeds, lower than 3 miles per hour, are identified and ranked as critical for expecting a complaint. Low wind days also contribute to finding that stable weather conditions tend to have higher frequency of odor complaints. Lowest ranked are days with strong wind speeds of 18 miles per hour or greater (Figure 79).

Rank	Beaufort Number	Wind Speed, mph	Description
Critical	5+	<3	Light calm
Severe	4	4-7	Light breeze
Substantial	3	8-12	Gentle breeze
Moderate	2	13-18	Moderate breeze
Low	0-1	>18	Strong breeze

Figure 79. Categories of Wind Speed Ranges Based on the Critical Level of Odor Complaint Occurrence

Receptors located directly downwind from the source have highest possibility of becoming sensitive to dispersed odors. Key receptor locations are ranked as follows:

1. Critical: Directly downwind
2. Severe: Slightly downwind (±45º)
3. Substantial: Crosswind (±90º)
4. Moderate: Slightly upwind (±135º)
5. Low: Directly upwind (±180º)

Warm and humid conditions enhance the human sense of smell so that odors are perceived more intensely. Dew point temperature was selected as a parameter to reflect the relationship between humidity and temperature. By knowing the values for temperature and relative humidity, a value

for dew point can be easily read from Table 45, which is adapted from the ASHRAE Psychrometric Chart.

Table 45. Relationship between Relative Humidity, Temperature and the Dew Point

Dew-Point Temperature (°F)															
Relative Humidity	Deign Dry Bulb Temperature (°F)														
	32°F	35°F	40°F	45°F	50°F	55°F	60°F	65°F	70°F	75°F	80°F	85°F	90°F	95°F	100°F
100%	32	35	40	45	50	55	60	65	70	75	80	85	90	95	100
90%	30	33	37	42	47	52	57	62	67	72	77	82	87	92	97
80%	27	30	34	39	44	49	54	58	64	68	73	78	83	88	93
70%	24	27	31	36	40	45	50	55	60	64	69	74	79	84	88
60%	20	24	28	32	36	41	46	51	55	60	65	69	74	79	83
50%	16	20	24	28	33	36	41	46	50	55	60	64	69	73	78
40%	12	15	18	23	27	31	35	40	45	49	53	58	62	67	71
30%	8	10	14	16	21	25	29	33	37	42	46	50	54	59	62
20%	6	7	8	9	13	16	20	24	28	31	35	40	43	48	52
10%	4	4	5	5	6	8	9	10	13	17	20	24	27	30	34
Adapted from ASHRAE Psychrometric Chart, 1993 ASHRAE Fundamentals Handbook															

As an example, if the temperature is 32ºF with relative humidity 80%, a dew-point temperature is equal to 27ºF. Temperature values higher than 75ºF are ranked as critical, while temperature vales below 50ºF as low potential for an odor episode (Figure 80).

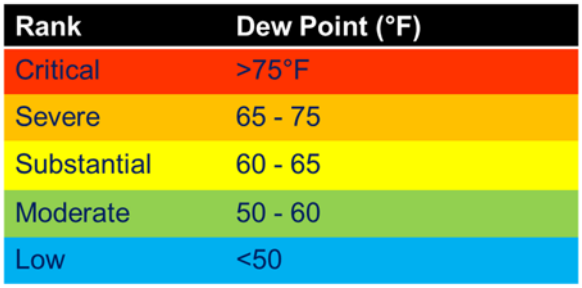

Figure 80. Categories of the Dew Point Temperatures Based on the Critical Level of Odor Complaint Occurrence

Rainfall accumulation from 3 days prior to an odor complaint was identified as a possible indicator for higher frequency of odor complaints. Days with more than 15 mm/hr of rain accumulation in a 3-day period reflect the scenario of torrential rainy days (Figure 81). Those levels of rainfall are categorized as critical for odor complaint occurrence. Dry days with accumulated levels of rainfall less than 0.5 mm/hr over a 3-day period are categorized as a low-level threat for odor complaint (Figure 81).

Rank	Precipitation Previous 3 days (mm/hr)	Descriptor
Critical	>15	Intense/torrential
Severe	7.5-15	Heavy
Substantial	2.5-7.5	Moderate
Moderate	0.5-2.5	Light
Low	<0.5	Dry

Figure 81. Categories of Precipitation Accumulated Previous 3 Days, Based on the Critical Level of Odor Complaint Occurrence

Atmospheric stability class could be identified by measuring the local adiabatic lapse rate, which is the rate of temperature change occurring with a rising or descending air parcel. The vertical temperature gradient is a function of elevation and temperature. The instability of the atmosphere increases as the temperature decreases with elevation. When the temperature decreases slowly, or even momentarily increases, with elevation- the atmosphere is considered stable. This information is highly site-specific and is rarely reported at weather stations unless they are located at airports, which publish hodographs showing wind vectors at altitude. At landfills, for example, the vertical temperature gradient could be collected using multiple temperature sensors: one on the hill (landfill body) and one at the ground level (fence line). In addition, iSense has proposed to collect balloon measurement devices or drone collected devices at landfill sites to collect this data. Since stable weather conditions (cloudy skies, low wind days) are related to more frequent odor complaints, those conditions were attributed with a higher level of threat for occurrence of odor complaints (Figure 82). An increase in temperature by more than 1.5ºC/100m is identified as strongly stable atmospheric class F, while a decrease in temperature by less than 1.9ºC/100m is considered as extremely unstable atmosphere class A ("Low" threat for odor complaints). Finally, the location of a temperature inversion layer must also be taken into consideration, since if an inversion layer is found aloft, then potential for fumigation of the ground level would increase the threat of odor complaints, while an inversion layer below the source would negate any threat to residents.

Rank	Pasquill-Gifford Scale	Vertical Temp Gradient $\Delta T/\Delta z$ (°C/100m)	Descriptor
Critical	F	> +1.5	Moderate/strongly stable
Severe	E	-0.5 to +1.5	Slightly stable
Substantial	D	-1.5 to -0.5	Neutral
Moderate	B-C	-1.9 to -1.5	Moderate/slightly unstable
Low	A	< -1.9	Extremely unstable

Figure 82. Categories of Atmospheric Stability Classes Based on the Critical Level of Odor Complaint Occurrence

Overnight pressure drop seems to be a useful indicator. However, more study is needed to develop useful scale. Low pressure days are considered as a "Critical" threat for occurrence of odor complaints (Figure 83).

Rank	Pressure drop	Descriptor
Critical		Low
Severe		Falling
Substantial		Neutral/normal
Moderate		Rising
Low		High

Figure 83. Categories for the Pressure Drop Based on the Critical Level of Odor Complaint Occurrence

Odor threat levels can be calibrated locally by solid waste personnel to adapt to their site specific conditions by taking into consideration their past experiences with odor issues and by identifying weather patterns characteristic to their specific site. Based on that, landfill site managers can change the bins within each threat level to better represent situations relevant to their location. An example of how odor threat levels can be used is presented in Table 46 (without the pressure drop category, which needs more development). Let's say the local conditions are as follows: wind speed is 1.5 mph, wind is blowing directly downwind from the odor source, temperature is 85ºF, precipitation is greater than 15 mm/hour, and the atmospheric stability class "F" or "moderately stable" is identified, the threat for a possible odor complaint is severe (all fields in red color).

Table 46. Example How to Use and Interpret "Odor Threat Levels"

WS	WD	DP	P	ASC	dP
5 mph	crosswind	72°F	1.5 mm/hr	D	-20 mbar?
<3	Directly downwind	>75°F	>15	F	
4 – 7	Slightly downwind	65 – 75	7.5 – 15	E	
8 – 12	Crosswind	60 – 65	2.5 –7.5	D	
13 – 18	Slightly upwind	50 – 60	0.5 –2.5	B-C	
>18	Directly upwind	<50	<0.5	A	

4.2.4 Alternative Technology Assessment

Once the source of odor is identified, a technology assessment can be performed to establish the preferred strategy to implement for odor control. Technologies considered in the assessment should be selected based on appropriate threshold criteria, such as minimum required removal efficiency of hydrogen sulfide, one of the most common odor causing compound recognized for generating odors at landfill site (Ko et al. 2015). Different sources of information should be accessed to gather valuable input, such as research journals, articles, U.S. EPA, and other landfills or industrial facilities practicing odor control. Since odor challenges are not exclusive to waste facilities, research articles related to technology assessment for odor control in wastewater treatment applications should also be considered. The criteria selected and ranked for the assessment should be based on sound engineering judgment, technical research, and valuable suggestions received from solid waste professionals. Some of the criteria selected could be related to:

- Odor Removal Efficiency: Technology with higher odor removal efficiency receives highest rank
- Frequency of Use: Importance of how often these technologies are successfully used in practice
- Cost Factors: Related to the capital cost and O&M cost; Detailed cost analysis should be supplied by the vendors; The technology with the lowest costs should be assigned with highest score in this criterion
- Energy Usage: Higher energy usage receives a lower score
- Land Footprint: Technology that requires smallest amount of land area receives higher score
- Chemical Requirements: Lower chemical necessity receives higher score, and
- Water Usage: Rewards those technologies that require the least amount of water for adequate performance

The scores for each of the technology options should be compiled, and an unweighted matrix constructed to identify the most preferred alternative with the highest score. Furthermore, a weighted matrix should be created by considering the assigned weight of each established criterion. The preferred option could be identified by the highest total score (unweighted and weighted), when compared to other technologies. Lastly, a sensitivity analyses should be performed by removing the highest ranked criterion since it has the highest weight on the final decision.

4.2.5 Biosensor Development

In this study, the amount of protein initially manufactured for testing allowed only three trials with hydrogen sulfide gas. To improve the predictive power of the linear model, more similar binding experiments should be conducted with higher and lower amounts of hydrogen sulfide. However, the ultimate purpose of this biosensor is to measure the intensity of a real air samples in close proximity to a landfill site that may result in an offensive odor. Therefore, it is vital that more experiments be conducted to establish linear regression models first with other pure odorants commonly found in landfills, then with mixtures of these gasses, and finally with field samples. Correlations would need to be made between odor levels at which most people find landfill odor

offensive and fluorescence intensity to create a predictive model that would ultimately make this biosensor an objective odor measurement tool.

The gas reactor was a first prototype of what could ultimately be a portable biosensor for use at landfill site. The design and construction could be improved in several ways. Ideally, the reaction chamber would be made of opaque, inert material such as acrylic or glass, and the one-way check-valves machined as part of the body of the chamber rather than being separate pieces to reduce leaks or contamination into the chamber. The reactor should minimize the volume of the biosensor complex and maximize the surface area exposed to the gas. A narrower cylinder may be an appropriate shape to serve these functions, since gas bubbles would travel upwards through the chamber. Rather than having to open the reaction chamber and insert a pipette to remove sample, a flow-through system would be preferable for delivering sample directly to the spectrofluorometer. Additionally, the spectrofluorometer component would need to be light in weight and stabilized on a platform for ease of mobility. One promising alternative option is shown in Figure 84.

Figure 84. 3-in-1 precision flow-through cuvette with screw connections made from 100% quartz (Hellma Analytics 2014)

Such a flow-through cuvette would address several challenges by: 1) allowing the biosensor complex and buffer to remain at a constant volume and concentration rather than changing due to samples being withdrawn, 2) preventing exposure to the external environment and potential contamination, 3) allowing for a smaller volume of buffer solution to be used, and 4) increasing speed and portability of measurements.

The current research did not as yet define the quantitation range of the sensor. Equilibrium dissociation constants of the biosensor complex should be established to determine the ratio of odorant-to-biosensor solution at which saturation occurs as well as the lowest concentration of odor the system can detect. Further exploration and verification of optimal parameters is necessary for future development of the biosensor. For example, the ideal ratio of hOBPIIa-to-1-AMA is still needed. Parameterization to find optimal settings for the spectrofluorometer, such as slit width, may be useful to achieve a more sensitive and accurate measurement.

Another unexplored aspect of the biosensor is the ability of the solution to be regenerated by changing the pH such that the biosensor complex releases the odorant molecules and then returning the pH to 7.5 to prepare for another round of measurement. Experiments exploring the regenerative

capacity of the biosensor solution would need to compare fluorescence readings before, during and after such pH changes and attempt to establish a limit to how many times regeneration could occur before altering the systems measurement capability. If a potassium phosphate buffer solution is used, the pH of the solution could be lowered using potassium phosphate and raised using potassium hydroxide.

Another important consideration is that changes in pH may occur to the buffer solution as a result of being exposed to acidic odorants. If such a pH change occurred, the binding capacity of the biosensor complex may change. Periodically measuring the pH of the buffer using a probe or a pH indicator added to the solution that would cause a color change in the event of a shift in pH might be an important modification to ensure optimal binding behavior of the biosensor complex.

4.2.6 Other Applications of Odorant Binding Protein to Odor Control

Another challenge facing solid waste processing facilities involves strong odors associated with tipping floors and observation decks (Curren et al. 2016). Operators and employees would benefit from the potential of an odorant binding protein solute ion to scavenge those odors from the environment. The protein solution could be periodically sprayed in these areas automatically at regular time intervals to scavenge the odors. There are several potential challenges to this scenario. One major issue would be establishing that the odorant binding solution is safe for human exposure at levels needed to scavenge the odors enough to effectively reduce them to more tolerable levels. Another issue is that the odorant binding solution would need to be strongly buffered such that the pH would not fall to the level that it may not bind the odorant molecules. Finally, the protein-odorant complex would need to be modified with a precipitation reaction or the protein would need to be immobilized onto some filtration media to ensure removal of the target odorant.

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MaxiMet

GMX600 Compact Weather Station

The MaxiMet range of compact weather stations is designed and manufactured by Gill Instruments. MaxiMet products use reliable, high quality instruments to provide accurate meteorological information in a wide variety of applications.

GMX600 Features

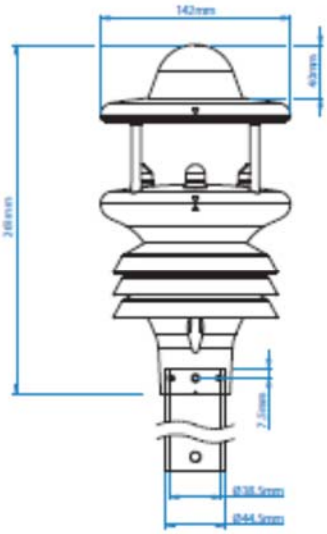
Temperature, humidity, pressure. A combined instrument mounted inside three double louvered, naturally aspirated radiation shields with no moving parts. The results are high performance across each measurement over long periods of time.

Wind. Wind speed and direction measurements are provided via an ultrasonic sensor and the addition of an electronic compass provides apparent wind measurements. Average speed and direction together with WMO averages and gust data is also provided. Add GPS (optional) to provide true wind and other features.

Precipitation. An integrated optical rain gauge that automatically senses water hitting its outside surface and provides measurements based on the size and number of drops. Algorithms interpret this data and simulate the output of a tipping bucket rain gauge in a serial format. The optical rain gauge has no moving parts associated with tipping bucket gauges.

TEMP, HUMIDITY & PRESSURE	PRECIPITATION	WIND	PARAMETERS
• Air Pressure / Temperature • Relative / Absolute humidity • Naturally aspirated UV stable Radiation shield • Protection against wind-blown precipitation/dust	• Rainfall total • Rainfall intensity • Rainfall Y/N • Emulated tipping bucket • Integrated heater • No moving parts	• Wind speed & direction • Apparent and true wind (with GPS) • WMO wind averages and gust • Compass • GPS (optional) gives height above sea level, latitude and longitude	• Temperature °C / °F / °K • Relative humidity % *Rh, g/m³, g/kg* • Barometric pressure *hPa, bar, mm Hg* • Wet bulb temperature °C / °F / °K • Absolute humidity *g/m³* • Air density *kg/m³* • Precipitation *mm/hr, mm/total, mm/24 hr in/hr, in/total, in/24 hr* • Wind speed *m/s, km/hr, mph, kts, ft/min* • Wind direction ° • Wind chill °C / °F / °K • True/apparent wind • Outputs *RS232, 422, 485 (ASCII), SDI-12, NMEA, MODBUS, Analogue (option)*

GPS (OPTION)
• Height above sea level m • Sunrise/sunset • Position of the sun • Twilight • MSL pressure



All MaxiMet Models Feature

- Quality Measurements
- Lightweight and Robust
- Low Power Mode
- Free of Charge Software
- Gill Proven Reliability
- Compact Integrated Design
- Real Time Output
- Easy Installation
- Gill Customer Support
- 2 Year Warranty

MaxiMet

GMX600 Compact Weather Station

Applications

- Building and Industrial Controls
- Authorities
- Transport
- Coastal
- Agricultural
- Safety
- Educational
- Commercial
- Energy

WIND SPEED	
Range	0.1 m/s to 60 m/s
Accuracy	± 3% to 40 m/s, ± 5% to 60 m/s
Resolution m/s	0.01
Starting Speed	0.1 m/s
Sampling Rate	1 Hz
Units	m/s, km/hr, mph, kts, ft/min

WIND DIRECTION	
Range	0-359°
Accuracy	± 3° to 40 m/s ± 5° to 60 m/s
Resolution	1°
Sampling Rate	1 Hz
Units	Degrees

TEMPERATURE	
Range	-40°C to +70°C
Resolution	0.1
Accuracy	± 0.3°C @ 20°C
Sampling Rate	1 Hz
Units	°C, °F, °K

HUMIDITY	
Range	0-100%
Resolution	1%
Accuracy	± 2% @ 20°C (10%-90% RH)
Sampling Rate	1 Hz
Units	% Rh, g/m3, g/Kg

DEW POINT	
Range	-40°C to +70°C
Resolution	0.1
Accuracy	± 0.3°C @ 20°C
Units	°C, °F, °K
Sampling Rate	1 Hz

PRESSURE	
Range	300 to 1100
Resolution	0.1 hPa
Accuracy	± 0.5 hPa @ 25°C
Sampling Rate	1 Hz
Units	hPa, bar, mmHg, inHg

PRECIPITATION	
Measurement type	Optical
Range	0 to >300 mm/hr
Precipitation Resolution	0.2 mm
Accuracy	2%
Sampling Rate	1 Hz
Units	mm/hr, mm/total, mm/24 hr, in/hr, in/total, in/24 hr
Heating	YES

OUTPUTS	
Output rate	1/s, 1/min, 1/hr
Digital Comms Modes	Serial RS232, RS422, RS485, SDI-12, NMEA, MODBUS, ASCII
Analogue Outputs	Available via separate optional device

POWER	
Power Supply	5 to 30 Vdc
Power (Nominal) 12 Vdc	80 mA continuous high mode. 0.7 mA eco-power mode (1 hour polled)

ENVIRONMENTAL CONDITIONS	
IP Rating	66
Operational Temperature Range	-40°C to +70°C
EMC Standard:	BS EN 61326 : 2013 FCC CFR47 parts 15.109
CE Marking	YES
RoHS compliant	YES
Weight	0.8 Kg
Origin	UK

Specifications may be subject to change without prior notice

GILL

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